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Department of Industry,  
Science and Resources

National  
Measurement  
Institute

# Proficiency Test Final Report AQA 25-15 Pesticides in River Water

December 2025

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Hamish Lenton  
Aaron Mamo  
Sofia Racomelara  
Scott Chen  
Lesley Johnston

Raluca Iavetz  
Manager, Chemical Reference Values  
105 Delhi Rd, North Ryde, NSW 2113, Australia  
Phone: +61 2 9449 0234  
Email: [proficiency@measurement.gov.au](mailto:proficiency@measurement.gov.au)



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## TABLE OF CONTENTS

SUMMARY	1
1 INTRODUCTION	2
1.1 NMIA Proficiency Testing Program	2
1.2 Study Aims	2
1.3 Study Conduct	2
2 STUDY INFORMATION	3
2.1 Study Timetable	3
2.2 Participation and Laboratory Code	3
2.3 Selection of Pesticides and Test Material Preparation	3
2.4 Homogeneity and Stability of Test Materials	4
2.5 Test Material Storage, Dispatch and Receipt	4
2.6 Instructions to Participants	4
2.7 Interim Report and Preliminary Report	5
3 PARTICIPANT LABORATORY INFORMATION	6
3.1 Participants' Test Methods	6
3.2 Basis of Participants' Measurement Uncertainty Evaluations	6
3.3 Participants' Comments	9
4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS	10
4.1 Results Summary	10
4.2 Outliers, Extreme Outliers and Other Excluded Results	10
4.3 Assigned Value	10
4.4 Robust Average and Robust Between-Laboratory Coefficient of Variation	10
4.5 Performance Coefficient of Variation	11
4.6 Standard Deviation for Proficiency Assessment	11
4.7 z-Score	11
4.8 E <sub>n</sub> -Score	11
4.9 Traceability and Measurement Uncertainty	12
5 TABLES AND FIGURES	13
6 DISCUSSION OF RESULTS	41
6.1 Assigned Value	41
6.2 Measurement Uncertainty Reported by Participants	41
6.3 z-Score	42
6.4 E <sub>n</sub> -Score	44
6.5 False Negatives	45
6.6 Reporting of Additional Analytes	46
6.7 Range of Pesticides Analysed by Participants	47
6.8 Participants' Analytical Methods	47
6.9 Certified Reference Materials	56
6.10 Summary of Participants' Results and Performances	56
6.11 Comparison with Previous Studies	61
7 REFERENCES	63
APPENDIX 1 SAMPLE PREPARATION	64
APPENDIX 2 ASSESSMENT OF HOMOGENEITY AND STABILITY	65
A2.1 Homogeneity	65
A2.2 Stability	65

APPENDIX 3	ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY, z-SCORE AND E <sub>n</sub> -SCORE CALCULATIONS	67
A3.1	Robust Average and Associated Uncertainty	67
A3.2	z-Score and E <sub>n</sub> -Score Calculation	67
APPENDIX 4	PARTICIPANTS' TEST METHODS	68
APPENDIX 5	ACRONYMS AND ABBREVIATIONS	90

## SUMMARY

This report presents the results of proficiency study AQA 25-15 Pesticides in River Water. There were a total of 35 participants, and all participants submitted results.

The sample set consisted of three river water samples. Samples were prepared in the Sydney NMIA laboratory using water from Browns Waterhole in New South Wales, Australia.

Of a possible 462 results, 268 numeric results (58%) were submitted. Fifty results were a 'less than' value ( $< x$ ) or Not Reported (NR), and 144 results were Not Tested (NT).

The assigned values for all scored analytes were the robust averages of participants' results. The associated uncertainties were evaluated from the robust standard deviations of the participants' results.

**Traceability:** The consensus of participants' results is not traceable to any external reference, so although expressed in SI units, metrological traceability has not been established.

The outcomes of the study were assessed against the aims as follows:

- *Assess the capabilities of participants to correctly identify environmentally significant pesticides in river water.*

Laboratory **23** reported numeric results for all scored analytes in this study.

Laboratories **6, 7, 9, 10, 12, 14, 20, 26, 27, 29, 30,** and **31** reported false negative ('less than' results where the assigned value was higher than their limit of reporting, or participants reporting NR; total of 23 results).

Twelve participants reported numeric results for analytes that were not spiked into the test samples by the study coordinator (total of 23 results).

- *Compare the performance of participants and assess their capabilities in the measurement of pesticides in river water.*

Laboratory performance was assessed using both  $z$ -scores and  $E_n$ -scores.

Of 222  $z$ -scores, 178 (80%) returned a score of  $|z| \leq 2.0$ , indicating an acceptable performance.

Of 216  $E_n$ -scores, 165 (76%) returned a score of  $|E_n| < 1.0$ , indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

- *Evaluate the participants' methods for the measurement of pesticides in river water.*

Participants reported a wide variety of methods to analyse the range of pesticides considered in this study. In this study, results returned by participants using SPE were generally biased low for the measurement of diuron.

Six participants reported correcting their results for recoveries.

- *Develop the practical application of measurement uncertainty, and provide participants with information that will be useful in assessing their uncertainty evaluations.*

Of 268 numeric results, 249 (93%) were reported with an expanded measurement uncertainty. The magnitude of reported uncertainties was within the range of 2.0% to 88%.

- *Produce materials that can be used in method validation and as control samples.*

The test samples of this proficiency study are homogeneous and are well characterised. Surplus samples are available for purchase and can be used for quality control and method validation purposes.

## **1 INTRODUCTION**

### **1.1 NMIA Proficiency Testing Program**

The National Measurement Institute Australia (NMIA) is responsible for Australia's national measurement infrastructure, providing a range of services including a chemical proficiency testing program.

Proficiency testing (PT) is the 'evaluation of participant performance against pre-established criteria by means of interlaboratory comparisons'.<sup>1</sup> NMIA PT studies target chemical testing in areas of high public significance such as trade, environment, law enforcement and food safety. NMIA offers studies in:

- per- and polyfluoroalkyl substances in soil, biosolids, water, biota, food, and consumables;
- hydrocarbons, phenols and other organic compounds in soil and water;
- pesticide residues in soil, water, fruit, vegetables, and herbs;
- metals in soil, water, food, filters, and paint;
- nutrients, anions and physical tests in water and soil;
- chlorophyll a in water; and
- controlled drug assay, drugs in wipes, and clandestine laboratory.

### **1.2 Study Aims**

The aims of the study were to:

- assess the capabilities of participants to correctly identify environmentally significant pesticides in river water;
- compare the performance of participants and assess their capabilities in the measurement of pesticides in river water;
- evaluate the participants' methods for the measurement of pesticides in river water;
- develop the practical application of measurement uncertainty, and provide participants with information that will be useful in assessing their uncertainty evaluations; and
- produce materials that can be used in method validation and as control samples.

The choice of the test method was left to the participating laboratories.

### **1.3 Study Conduct**

The conduct of NMIA proficiency tests is described in the NMIA Study Protocol for Proficiency Testing.<sup>2</sup> The statistical methods used are described in the NMIA Chemical Proficiency Testing Statistical Manual.<sup>3</sup> These documents have been prepared with reference to ISO/IEC 17043,<sup>1</sup> and the International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories.<sup>4</sup>

NMIA is accredited by the National Association of Testing Authorities, Australia (NATA) to ISO/IEC 17043 as a provider of proficiency testing schemes.<sup>1</sup> This study falls within the scope of NMIA's accreditation.

## 2 STUDY INFORMATION

### 2.1 Study Timetable

The timetable of the study was:

Invitations sent	11/08/2025
Samples sent	1/09/2025
Results due	10/10/2025
Interim Report	16/10/2025
Preliminary Report	20/10/2025

### 2.2 Participation and Laboratory Code

Thirty-two laboratories registered to participate in this study. Two laboratories requested multiple sets of test samples to be analysed by different analysts and/or methods, resulting in a total of 35 participants in the study. All participants were assigned a confidential laboratory code number for this study. All participants submitted results.

### 2.3 Selection of Pesticides and Test Material Preparation

When selecting matrices and spiking values for this study, consideration was given to:

- a variety of pesticides (amenable to gas and/or liquid chromatography); and
- the National Environment Protection (Assessment of Site Contamination) Measure Schedule B1 *Guideline on Investigation Levels for Soil and Groundwater*.<sup>5</sup>

Samples were prepared by spiking river water with various pesticides to obtain the concentrations listed in Table 1. Additional information on the preparation of the samples is given in Appendix 1.

Table 1 Spiked Values of Test Samples

Sample	Analyte	Spiked Value (µg/L)	Uncertainty* (µg/L)
S1	Aldrin	18.2	0.9
	Diuron	3.68	0.18
	Fenitrothion	1.30	0.06
	Fenthion	30.0	1.5
	Imazapyr	21.0	1.0
	Metolachlor	0.490	0.024
S2	Atrazine	2.49	0.12
	Deltamethrin	19.1	1.0
	Diazinon	0.251	0.013
	Dimethoate	16.9	0.8
	Fenthion	3.02	0.15
	Metsulfuron-methyl	3.52	0.18
S3	AMPA	7.11	0.36
	Glyphosate	3.00	0.15

\*Expanded uncertainty at approximately 95% confidence using a coverage factor of 2. This has been evaluated with consideration to contributions from the gravimetric and volumetric operations involved in spiking, and the purity of the pesticide reference standards. Stability was not considered in the uncertainty budget and so the expanded uncertainty is related to the concentration of the pesticides at the time of spiking.

## 2.4 Homogeneity and Stability of Test Materials

No homogeneity or stability testing was conducted before the samples were sent. The samples were prepared, packaged, stored and dispatched using a process that has been demonstrated to produce sufficiently homogeneous and stable samples in previous NMIA Pesticides in River Water PT studies. Participants' results gave no reason to question the homogeneity or transportation stability of the samples (Appendix 2).

To further assess possible instability, the results returned by participants were compared to the spiked values. Assigned values for all scored analytes were within 54% to 104% of the spiked values, which is similar to what has been observed in previous NMIA Pesticides in River Water studies.

## 2.5 Test Material Storage, Dispatch and Receipt

After preparation, the samples were stored at 4°C. Samples were packaged into insulated polystyrene foam boxes with cooler bricks and dispatched by courier on 1 September 2025.

The following items were packaged with the samples:

- a covering letter which included a description of the test samples and instructions for participants; and
- a form for participants to confirm the receipt and condition of the test samples.

An Excel spreadsheet for the electronic reporting of results was emailed to participants.

## 2.6 Instructions to Participants

Participants were provided with a list of analytes (Table 2) that were potentially spiked into Samples S1 and S2, and were informed that Sample S3 was spiked with AMPA and glyphosate.

Table 2 List of Possible Analytes for Samples S1 and S2

Acetamiprid	p,p'-DDE	Lindane
Aldricarb	p,p'-DDT	Malathion
Aldrin	Total DDT	MCPA
Atrazine	Deltamethrin	Parathion
Azinphos-methyl	Diazinon	Metolachlor
cis-Chlordane	Dichlorvos	Metsulfuron-methyl
trans-Chlordane	Dieldrin	Pendimethalin
Total Chlordane	Dimethoate	Permethrin
Chlorfenvinphos	Diuron	Picloram
Chlorpyrifos	Endosulfan sulfate	Piperonyl butoxide
Clopyralid	Ethion	Pirimicarb
Cyfluthrin	Fenitrothion	Pirimiphos-ethyl
Cypermethrin	Fenthion	Pirimiphos-methyl
2,4-D	Heptachlor	Propiconazole
Diazinon	Hexazinone	Simazine
p,p'-DDD	Imazapyr	Tetrachlorvinphos

Participants were instructed as follows:

- Quantitatively analyse the samples using your routine test method.
- Participants need not test for all listed analytes.
- If analyses cannot be commenced on the day of receipt, please store the samples chilled.
- For each analyte in each sample, report a single result in units of  $\mu\text{g/L}$  expressed as if reporting to a client (i.e. corrected for recovery or not, according to your standard procedure). This figure will be used in all statistical analysis in the study report.
- For each analyte in each sample, report the associated expanded uncertainty in units of  $\mu\text{g/L}$  (e.g.  $0.50 \pm 0.02 \mu\text{g/L}$ ), if determined.
- No limit of reporting has been set for this study. Report results as you would to a client, applying the limit of reporting of the method used for analysis.
- Report any listed pesticide not tested as NT.
- Give details of your methodology and basis of uncertainty evaluation as requested by the results sheet emailed to you.
- If determined, report your percentage recovery. This will be presented in the report for information only.
- Return the completed results sheet by 26 September 2025 by email to [proficiency@measurement.gov.au](mailto:proficiency@measurement.gov.au).

The results due date was extended to 10 October 2025 in response to several participants' requests, due to staffing and analysis constraints.

## **2.7 Interim Report and Preliminary Report**

An Interim Report was emailed to all participants on 16 October 2025.

A Preliminary Report was emailed to all participants on 20 October 2025. This report included a summary of the results reported by participants, assigned values, performance coefficients of variation (PCVs),  $z$ -scores and  $E_n$ -scores for each analyte in this study. No data from the Preliminary Report has been changed in the present Final Report.

### 3 PARTICIPANT LABORATORY INFORMATION

#### 3.1 Participants' Test Methods

Participants were requested to provide information about their test methods. Responses are presented in Appendix 4.

#### 3.2 Basis of Participants' Measurement Uncertainty Evaluations

Participants were requested to provide information about the basis of their measurement uncertainty (MU) evaluations. Responses are presented in Tables 3 and 4. Some responses may be modified so that the participant cannot be identified.

Table 3 Basis of Measurement Uncertainty Evaluation

Lab. Code	Approach to Evaluating MU	Information Sources for MU Evaluation*		Guide Document for Evaluating MU
		Precision	Method Bias	
1	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples - CRM Duplicate analysis Instrument calibration	CRM Instrument calibration	Eurachem/CITAC Guide
2	Bottom Up (ISO/GUM, fish bone/cause and effect diagram) Coverage factor not reported	Control samples – RM / Ex PT Sample Duplicate analysis Instrument calibration	CRM Instrument calibration Laboratory bias from PT studies Recoveries of SS Standard purity	ISO/GUM
3	Top Down - precision and evaluation of the method and laboratory bias Coverage factor not reported	Control samples Duplicate analysis Instrument calibration	Instrument calibration	Eurachem/CITAC Guide
4	Coverage factor not reported	Control samples - CRM Duplicate analysis		
5	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples - SS Duplicate analysis	CRM Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
6	Standard deviation of replicate analyses multiplied by 2 or 3 k = 2	Control samples	Recoveries of SS	
7	Coverage factor not reported	Control samples Duplicate analysis	Laboratory bias from PT studies Recoveries of SS Standard purity	ISO/GUM
8**	Standard deviation of replicate analyses multiplied by 2 k = 2	Control samples - SS	Recoveries of SS	Statistics and Chemometrics for Analytical Chemistry, Miller and Miller, 5th Edition
9	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide

Lab. Code	Approach to Evaluating MU	Information Sources for MU Evaluation*		Guide Document for Evaluating MU
		Precision	Method Bias	
10	Bottom Up (ISO/GUM, fish bone/cause and effect diagram) k = 2	Duplicate analysis	Recoveries of SS	ISO/GUM
11	Top Down - precision and evaluation of the method and laboratory bias Coverage factor not reported	Control samples - SS		
12	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples - SS Duplicate analysis	Instrument calibration Recoveries of SS	ISO/GUM
13	Standard deviation of replicate analyses multiplied by 2 or 3 Coverage factor not reported	Standard deviation from PT studies only		Eurachem/CITAC Guide
		Control samples - SS Duplicate analysis Instrument calibration	Recoveries of SS	
14	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples - CRM Duplicate analysis Instrument calibration	CRM Instrument calibration Standard purity	NMIA Uncertainty Course
15	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples - CRM	CRM	Eurachem/CITAC Guide
16	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples - CRM Duplicate analysis	CRM Recoveries of SS	ISO/GUM
17	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples – RM / Ex PT Sample Duplicate analysis	CRM Instrument calibration Recoveries of SS	NMIA Uncertainty Course
18	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples - SS Instrument calibration	Instrument calibration Recoveries of SS Standard purity	Eurachem/CITAC Guide
19	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples - CRM Duplicate analysis Instrument calibration	CRM	NMIA Uncertainty Course
20	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide
21	Standard deviation of replicate analyses multiplied by 2 or 3 k = 2	Control samples - SS Duplicate analysis	Recoveries of SS	Eurachem/CITAC Guide

Lab. Code	Approach to Evaluating MU	Information Sources for MU Evaluation*		Guide Document for Evaluating MU
		Precision	Method Bias	
22**	Standard deviation of replicate analyses multiplied by 2 or 3 k = 2	Control samples - SS Duplicate analysis	Instrument calibration Standard purity	Eurachem/CITAC Guide
23	Based on repeatability k = 2.26	Control samples - SS Duplicate analysis	Recoveries of SS	Eurachem/CITAC Guide
24	Black Box k = 2	Control samples - SS Duplicate analysis Instrument calibration	Standard purity	ISO/GUM
25	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples - CRM Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS Standard purity	NMIA Uncertainty Course
26	Top Down - precision and evaluation of the method and laboratory bias Coverage factor not reported	Control samples - CRM Duplicate analysis	CRM Recoveries of SS	Eurachem/CITAC Guide
27	Top Down - precision and evaluation of the method and laboratory bias Coverage factor not reported	Control samples Duplicate analysis	Laboratory bias from PT studies Recoveries of SS Standard purity	ISO/GUM
28	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples - SS Duplicate analysis Instrument calibration	Recoveries of SS	Eurachem/CITAC Guide
29	Coverage factor not reported			
30	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide
31	Top Down - precision and evaluation of the method and laboratory bias Coverage factor not reported	Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	ISO/GUM
32	Coverage factor not reported	Control samples - CRM Duplicate analysis		
33	Coverage factor not reported	Control samples - CRM Duplicate analysis		
34	Top Down - precision and evaluation of the method and laboratory bias Coverage factor not reported	Duplicate analysis		Eurachem/CITAC Guide
35**	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples - SS Duplicate analysis	CRM Instrument calibration Standard purity	In-house quality procedures

\*SS = Spiked Samples, RM = Reference Material, CRM = Certified Reference Material

\*\*Additional information in Table 4.

Table 4 Basis of Measurement Uncertainty Evaluation – Additional Information

Lab. Code	Additional Information
8	Measurement Uncertainty (U) estimated from the standard deviation (u) of replicate recovery samples using the expression $U = 2 \times u$ .
22	For Sources for precision above, Control Samples was selected as the laboratory does perform a Laboratory Control Spike (LCS) and a Sample Matrix Spike as part of our in-house QC procedure. However, sample spikes are not typically performed on PT samples.
35	Uncertainty for this particular method not well established at this stage. Participation in this proficiency test makes up part of the initial validation of this method

### 3.3 Participants' Comments

Participants were invited to make any comments or suggestions on the samples, this study, or possible future studies. Such feedback may be useful in improving future studies.

Participants' comments received for this study are presented in Table 5; some responses may be modified so that the participant cannot be identified.

Table 5 Participants' Comments

Lab. Code	Participant's Comments	Study Coordinator's Response
35	Would be great if this could become an on-demand rapid one. Also, the same goes for organotins, pharmaceuticals and hormones in water / wastewater	Thank you very much for your feedback. We will continue to investigate which studies are suitable as rapid PT studies, including reviewing pesticides in water, and we encourage laboratories to let us know if they have any requests. We will consider your analyte and matrix suggestions for the design of future studies.

## 4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

### 4.1 Results Summary

Participant results are listed in Tables 6 to 19 with summary statistics: robust average, median, mean, number of numeric results (N), maximum (Max), minimum (Min), robust standard deviation (Robust SD) and robust coefficient of variation (Robust CV), as well as other estimates of analyte concentration. Bar charts of results and performance scores are presented in Figures 2 to 15. An example chart with interpretation guide is shown in Figure 1.

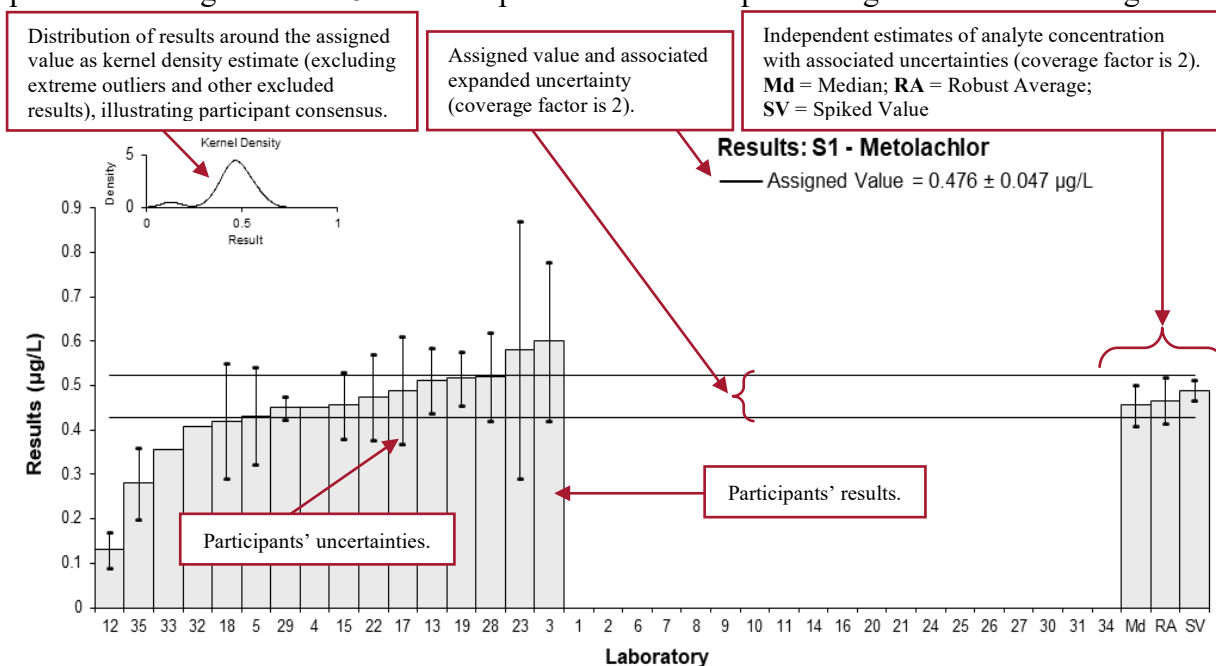


Figure 1 Guide to Presentation of Results

### 4.2 Outliers, Extreme Outliers and Other Excluded Results

Outliers were results less than 50% and greater than 150% of the robust average, and these were removed before the calculation of the assigned value, if applicable.<sup>3,4</sup> Extreme outliers (gross errors), such as those due to incorrect units, decimal placement errors, or results for a different PT item, were also removed for the calculation of all summary statistics.<sup>3</sup>

The results reported by Laboratory 12 in Sample S3 were consistently higher than the assigned value by approximately the same factor. The results reported by Laboratory 35 in Samples S1 and S2 were also consistently low. To avoid unfair scoring, these results were excluded from the robust average calculations as they would bias the assigned value; they were also excluded from the calculation of all summary statistics.

### 4.3 Assigned Value

The assigned value is defined as the 'value attributed to a particular property or characteristic of a proficiency test item'.<sup>1</sup> In this PT study, this property is the concentration of the analytes in the samples. Assigned values were the robust averages of participants' results, and the expanded uncertainties were evaluated from the associated robust SDs (Appendix 3).

### 4.4 Robust Average and Robust Between-Laboratory Coefficient of Variation

The robust averages and associated expanded uncertainties, and robust CVs (a measure of the variability of participants' results) were calculated using the procedure described in ISO 13528.<sup>6</sup>

#### 4.5 Performance Coefficient of Variation

The performance coefficient of variation (PCV) is a fixed measure of the between-laboratory variation that in the judgement of the study coordinator would be expected from participants given the analyte concentrations. The PCV is not the CV of participants' results; it is set by the study coordinator, is based on the analyte concentrations and experience from previous studies, and is supported by mathematical models such as the Thompson-Horwitz equation.<sup>7</sup> By setting a fixed and realistic value for the PCV, a participant's performance does not depend on other participants' performances and can be compared from study to study.

#### 4.6 Standard Deviation for Proficiency Assessment

The standard deviation for proficiency assessment (SDPA,  $\sigma$ ) is the product of the assigned value ( $X$ ) and the PCV, as presented in Equation 1.

$$\sigma = X \times PCV \quad \text{Equation 1}$$

#### 4.7 z-Score

For each participant result, a z-score is calculated according to Equation 2.

$$z = \frac{(\chi - X)}{\sigma} \quad \text{Equation 2}$$

where:

- $z$  is z-score
- $\chi$  is a participant's result
- $X$  is the assigned value
- $\sigma$  is the SDPA from Equation 1

For the absolute value of a z-score:

- $|z| \leq 2.0$  is acceptable;
- $2.0 < |z| < 3.0$  is questionable; and
- $|z| \geq 3.0$  is unacceptable.

To account for potential low bias in consensus value due to inefficient methodologies, scores may be adjusted for a 'maximum acceptable result' (see Section 6.3 for more information).

#### 4.8 $E_n$ -Score

The  $E_n$ -score is complementary to the z-score in assessment of laboratory performance. The  $E_n$ -score includes measurement uncertainty and is calculated according to Equation 3.

$$E_n = \frac{(\chi - X)}{\sqrt{U_\chi^2 + U_X^2}} \quad \text{Equation 3}$$

where:

- $E_n$  is  $E_n$ -score
- $\chi$  is a participant's result
- $X$  is the assigned value
- $U_\chi$  is the expanded uncertainty of the participant's result
- $U_X$  is the expanded uncertainty of the assigned value

For the absolute value of an  $E_n$ -score:

- $|E_n| < 1.0$  is acceptable; and
- $|E_n| \geq 1.0$  is unacceptable.

#### **4.9 Traceability and Measurement Uncertainty**

Laboratories accredited to ISO/IEC 17025 must establish and demonstrate the traceability and MU associated with their test results.<sup>8</sup> Guidelines for quantifying uncertainty in analytical measurement are described in the Eurachem/CITAC Guide.<sup>9</sup>

## 5 TABLES AND FIGURES

Table 6

### Sample Details

<b>Sample No.</b>	S1
<b>Matrix</b>	River Water
<b>Analyte</b>	Aldrin
<b>Unit</b>	µg/L

### Participant Results

Lab. Code	Result	Uncertainty	Rec
1	1.1	0.3	96
2	0.7	0.51	NR
3	1.2	0.36	NR
4	4.3615	NT	109
5	1.954	0.586	NR
6	4.09	0.53	93
7	0.27	0.081	70
8	NS	NS	NS
9	3.6	2	NR
10	1.06	0.32	NR
11	0.97	0.68	NR
12	0.81	0.24	NR
13	NT	NT	NT
14	2	0.6	NR
15	1.073	0.140	NR
16	2.12	0.64	88
17	NT	NT	NT
18	4.3	1.2	NR
19	2.45	1	NR
20	1.7	0.5	NR
21	2.2	0.75	NR
22	1.52	0.69	NR
23	1.2	0.6	50
24	NT	NT	NT
25	2.2	0.66	NR
26	1.52	0.46	NR
27	2.3	0.575	70
28	2.9	0.58	NR
29	1.5	0.19	116
30	1.1	0.3	80-120
31	0.55	0.17	133
32	4.6132	NT	111
33	3.2985	NT	109
34	3.93	1.2	73
35	NT	NT	NT

### Statistics

<b>Assigned Value</b>	Not Set	
<b>Spike Value</b>	18.2	0.9
<b>Robust Average</b>	2.05	0.61
<b>Median</b>	1.83	0.50
<b>Mean</b>	2.09	
<b>N</b>	30	
<b>Max</b>	4.6132	
<b>Min</b>	0.27	
<b>Robust SD</b>	1.3	
<b>Robust CV</b>	66%	

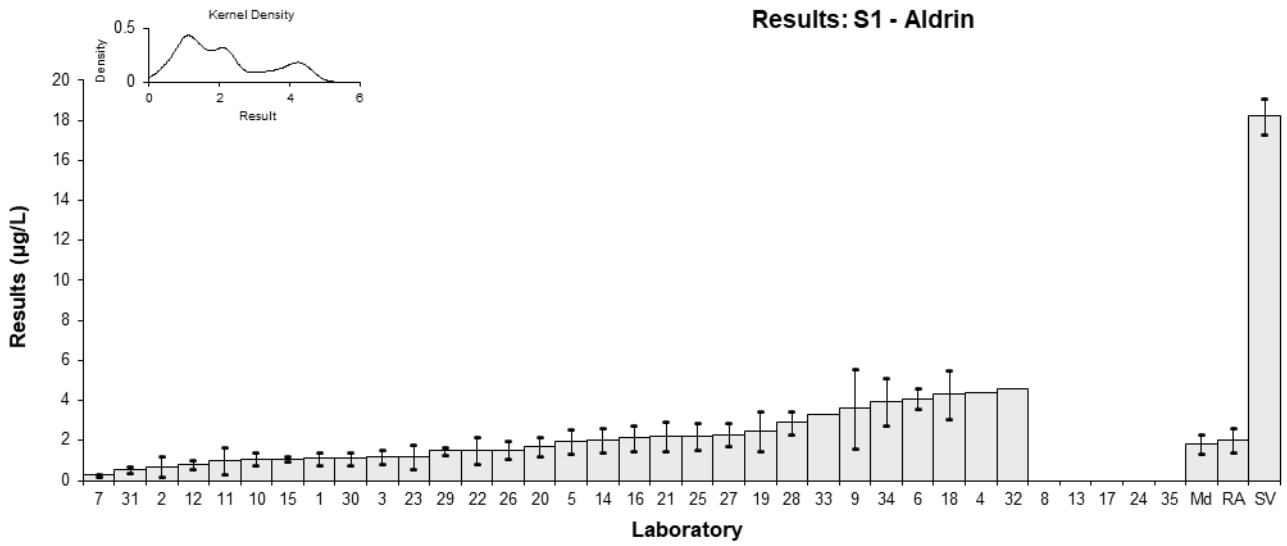


Figure 2

Table 7

## Sample Details

<b>Sample No.</b>	S1
<b>Matrix</b>	River Water
<b>Analyte</b>	Diuron
<b>Unit</b>	µg/L

## Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E <sub>n</sub>
1	NT	NT	NT		
2	NT	NT	NT		
3	4.5	1.35	NR	2.45	0.86
4*	1.3204	NT	72	-3.99	-4.69
5	4.12	1.03	NR	1.68	0.75
6	<1	NR	NR		
7	2.9	0.87	76	-0.79	-0.40
8	NS	NS	NS		
9	NT	NT	NT		
10	3.33	0.8	NR	0.08	0.04
11	NT	NT	NT		
12	3.2	0.35	NR	-0.18	-0.16
13	2.71	0.306	42	-1.18	-1.12
14	3.1	0.93	NR	-0.39	-0.19
15	3.98	0.758	NR	1.40	0.80
16	NT	NT	NT		
17	3.81	0.95	88	1.05	0.50
18	3.25	0.85	NR	-0.08	-0.04
19	3.595	1	NR	0.62	0.28
20	3	1	NR	-0.59	-0.27
21	NT	NT	NT		
22	3.6	1.5	NR	0.63	0.20
23	4.1	2.05	100	1.64	0.39
24	NT	NT	NT		
25	< 5	NR	NR		
26	NT	NT	NT		
27	1.9	0.475	76	-2.82	-2.19
28	2.7	0.54	NR	-1.20	-0.86
29	3.0	0.062	92	-0.59	-0.68
30	NT	NT	NT		
31	NR	NR	NR		
32*	1.3503	NT	76	-3.93	-4.62
33	2.0571	NT	72	-2.50	-2.94
34	NT	NT	NT		
35**	1.6	0.2	95	-3.42	-3.63

\* Outlier, \*\* Excluded Result, see Section 4.2

## Statistics

<b>Assigned Value</b>	3.29	0.42
<b>Spike Value</b>	3.68	0.18
<b>Robust Average</b>	3.12	0.51
<b>Median</b>	3.15	0.37
<b>Mean</b>	3.08	
<b>N</b>	20	
<b>Max</b>	4.5	
<b>Min</b>	1.3204	
<b>Robust SD</b>	0.92	
<b>Robust CV</b>	29%	

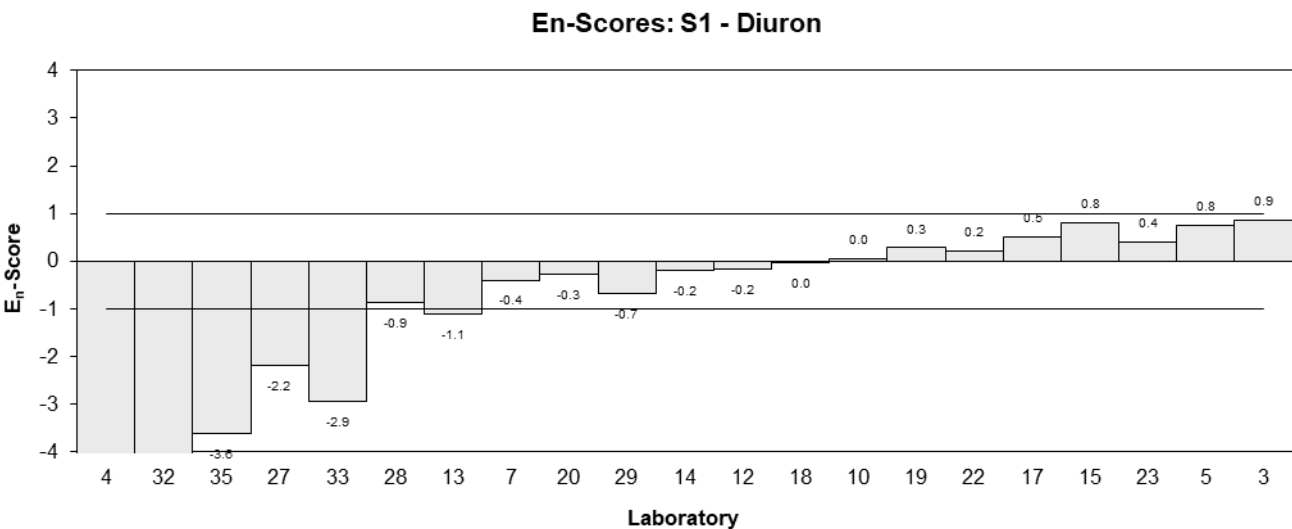
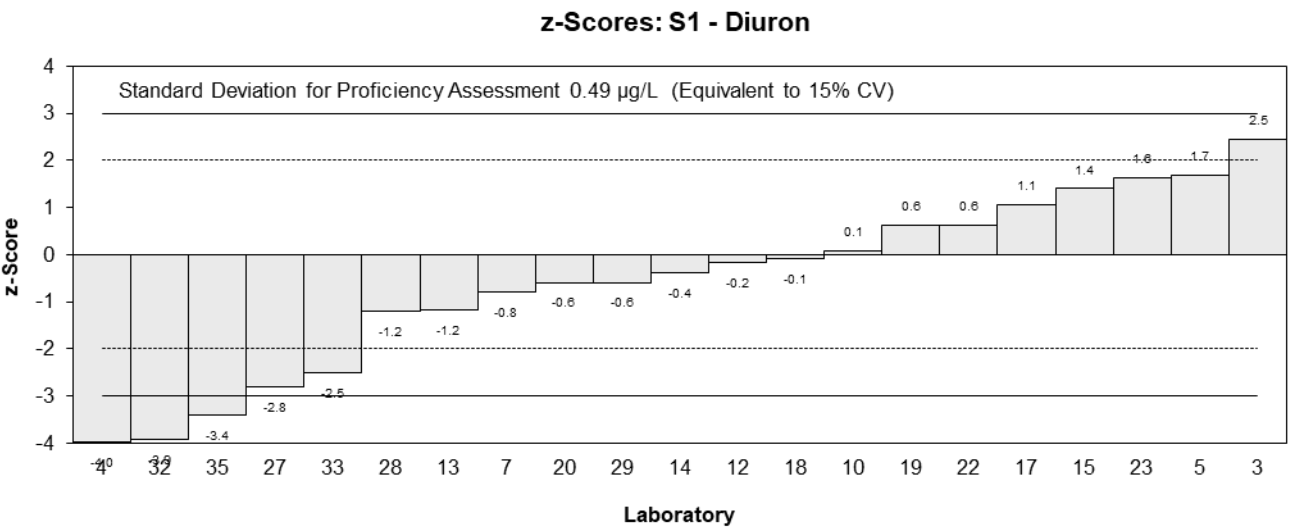
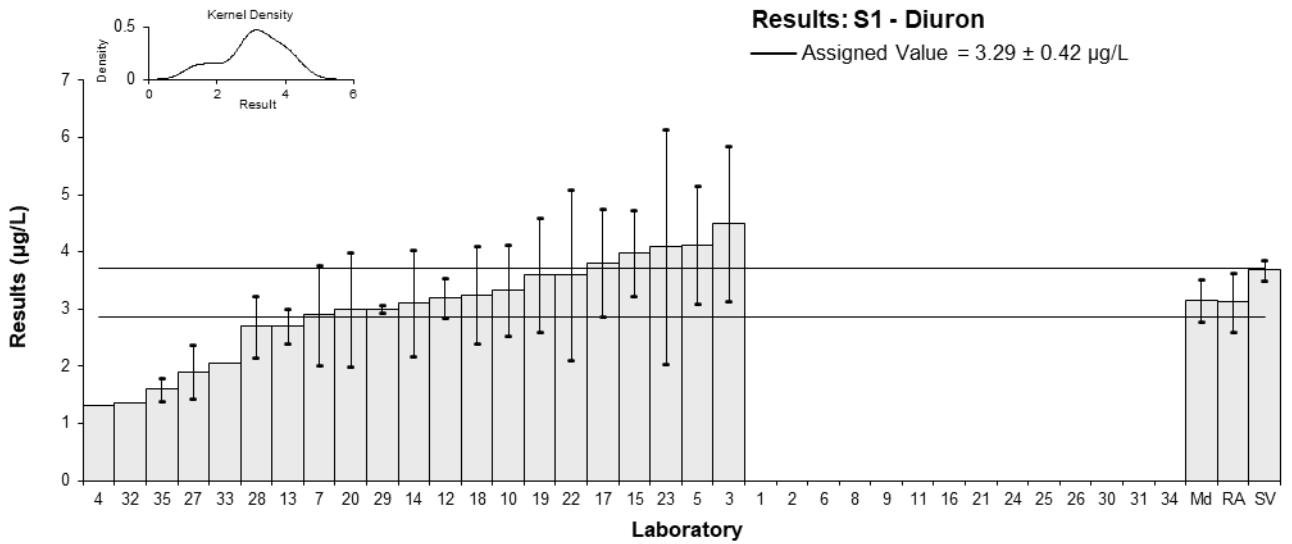


Figure 3

Table 8

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix</b>	River Water
<b>Analyte</b>	Fenitrothion
<b>Unit</b>	µg/L

**Participant Results**

Lab. Code	Result	Uncertainty	Rec	z	E <sub>n</sub>
1	NT	NT	NT		
2	NT	NT	NT		
3	NT	NT	NT		
4	NT	NT	NT		
5	<2	NR	NR		
6	<1	NR	NR		
7*	0.52	0.156	125	-3.54	-2.73
8	NS	NS	NS		
9	1	0.7	NR	-0.66	-0.15
10	1.12	0.29	NR	0.06	0.03
11	< 2	NR	NR		
12	<0.01	NR	NR		
13	NT	NT	NT		
14	< 0.01	NR	NR		
15	<2	0.920	NR		
16	1.42	0.43	103	1.86	0.68
17	NT	NT	NT		
18	NT	NT	NT		
19	<2.5	NR	NR		
20	1	0.3	NR	-0.66	-0.33
21	1.2	0.14	NR	0.54	0.44
22	1.21	0.37	NR	0.60	0.25
23	1.3	0.65	91	1.14	0.28
24	NT	NT	NT		
25	< 2	NR	NR		
26	<0.5	NR	NR		
27	0.88	0.22	125	-1.38	-0.86
28	0.89	0.18	NR	-1.32	-0.94
29	<1	NR	NR		
30	1	0.3	80-120	-0.66	-0.33
31	<2	NR	NR		
32	NT	NT	NT		
33	NT	NT	NT		
34	1.25	0.4	97	0.84	0.33
35	NT	NT	NT		

\* Outlier, see Section 4.2

**Statistics**

<b>Assigned Value</b>	1.11	0.15
<b>Spike Value</b>	1.30	0.06
<b>Robust Average</b>	1.08	0.16
<b>Median</b>	1.06	0.17
<b>Mean</b>	1.07	
<b>N</b>	12	
<b>Max</b>	1.42	
<b>Min</b>	0.52	
<b>Robust SD</b>	0.22	
<b>Robust CV</b>	21%	

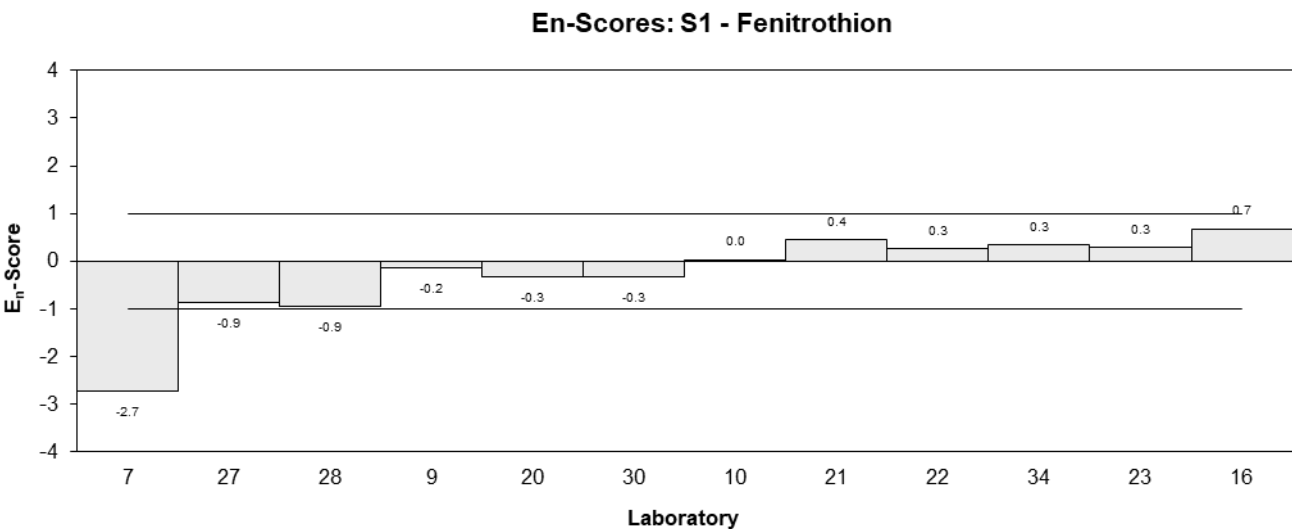
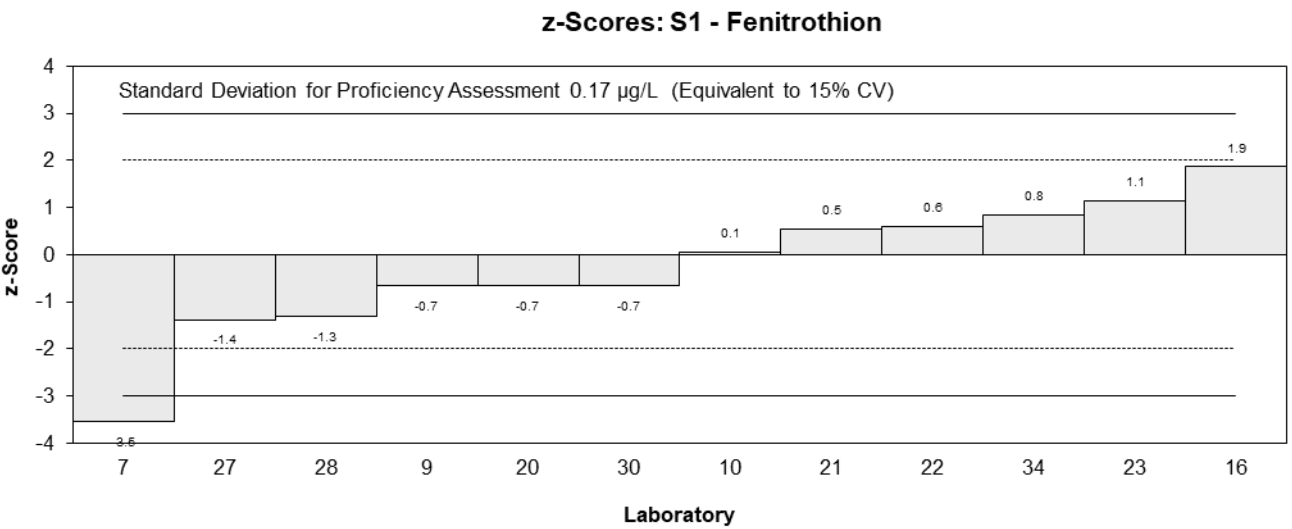
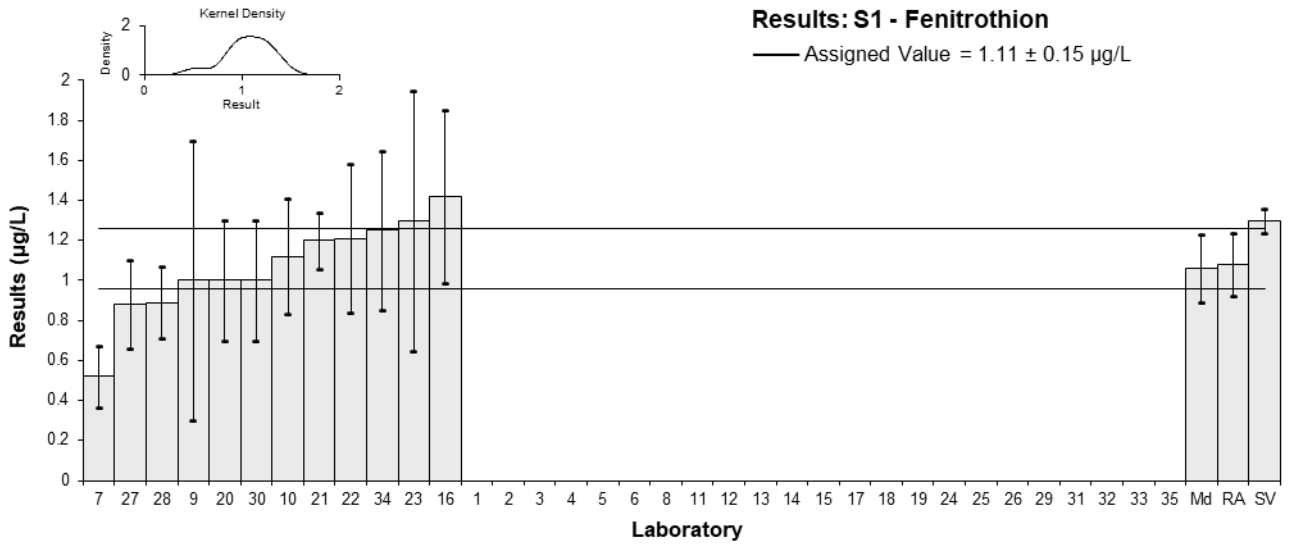


Figure 4

Table 9

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix</b>	River Water
<b>Analyte</b>	Fenthion
<b>Unit</b>	µg/L

**Participant Results**

Lab. Code	Result	Uncertainty	Rec	z	E <sub>n</sub>
1	24.1	6.3	96	-0.32	-0.17
2	14.2	10.58	NR	-2.92	-1.01
3	NT	NT	NT		
4	NT	NT	NT		
5	28.2	5.64	NR	0.76	0.45
6	NT	NT	NT		
7	25.2	7.56	116	-0.03	-0.01
8	NS	NS	NS		
9	20	7	NR	-1.40	-0.70
10	31.6	6.94	NR	1.66	0.83
11	23.5	7.52	NR	-0.47	-0.22
12*	12.19	3.6	NR	-3.45	-2.80
13	35.17	7.23	22	2.60	1.26
14	27.9	8.37	NR	0.69	0.29
15	20.6	2.540	NR	-1.24	-1.20
16	33.2	10	100	2.08	0.76
17	NT	NT	NT		
18	NT	NT	NT		
19	29.5	6	NR	1.11	0.63
20	22	7	NR	-0.87	-0.43
21	NT	NT	NT		
22	NT	NT	NT		
23	31	15.5	97	1.50	0.36
24	NT	NT	NT		
25	25.6	7.68	NR	0.08	0.04
26	25.6	5.7	NR	0.08	0.05
27	18	4.5	116	-1.92	-1.35
28	21	4.2	NR	-1.13	-0.83
29	24	1.3	92	-0.34	-0.40
30	21	4	80-120	-1.13	-0.86
31	28	8.4	129	0.71	0.30
32	NT	NT	NT		
33	NT	NT	NT		
34	NT	NT	NT		
35	NT	NT	NT		

\* Outlier, see Section 4.2

**Statistics**

<b>Assigned Value</b>	25.3	3.0
<b>Spike Value</b>	30.0	1.5
<b>Robust Average</b>	24.8	3.2
<b>Median</b>	24.7	2.9
<b>Mean</b>	24.6	
<b>N</b>	22	
<b>Max</b>	35.17	
<b>Min</b>	12.19	
<b>Robust SD</b>	5.9	
<b>Robust CV</b>	24%	

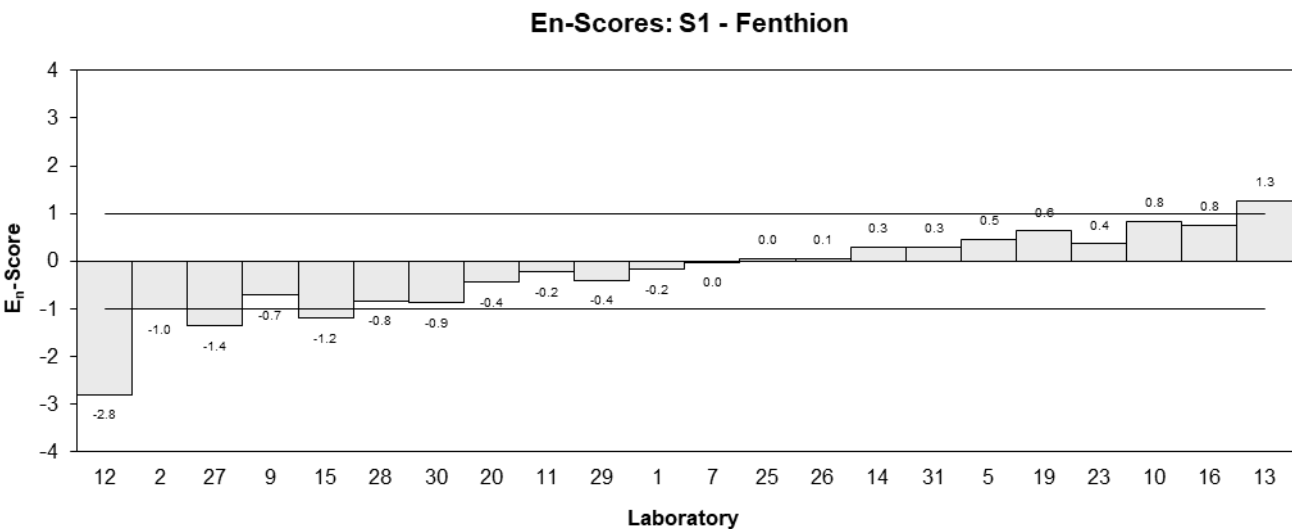
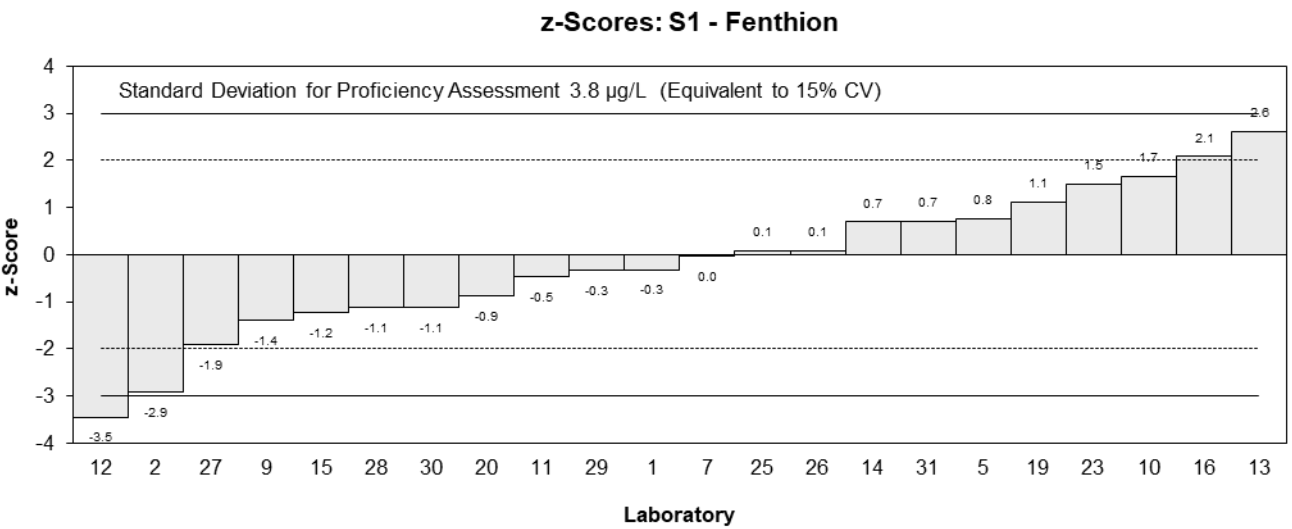
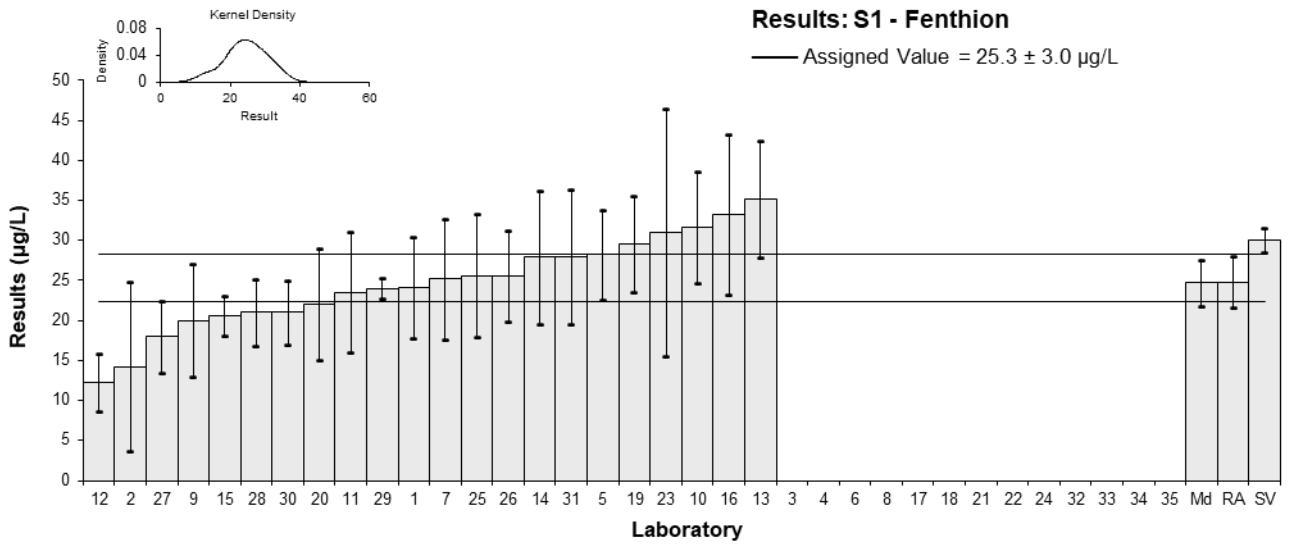


Figure 5

Table 10

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix</b>	River Water
<b>Analyte</b>	Imazapyr
<b>Unit</b>	µg/L

**Participant Results**

Lab. Code	Result	Uncertainty	Rec	z	E <sub>n</sub>
1	NT	NT	NT		
2	NT	NT	NT		
3	NT	NT	NT		
4	NT	NT	NT		
5	NT	NT	NT		
6	NT	NT	NT		
7	13	3.9	116	-2.65	-1.39
8	NS	NS	NS		
9	NT	NT	NT		
10	NT	NT	NT		
11	NT	NT	NT		
12	25.7	3.8	NR	1.27	0.67
13**	0.371	0.102	81	-6.55	-4.42
14	29.19	8.76	NR	2.34	0.76
15	21.9	3.870	NR	0.09	0.05
16	NT	NT	NT		
17	24.43	6.11	102	0.87	0.36
18	23.6	7.1	NR	0.62	0.23
19	NT	NT	NT		
20	22	7	NR	0.12	0.05
21	NT	NT	NT		
22	NT	NT	NT		
23	25	12.5	120	1.05	0.25
24	NT	NT	NT		
25	NT	NT	NT		
26	NT	NT	NT		
27	13	3.25	116	-2.65	-1.48
28	NT	NT	NT		
29	18	0.91	106	-1.11	-0.74
30	NT	NT	NT		
31	NR	NR	NR		
32	NT	NT	NT		
33	NT	NT	NT		
34	NT	NT	NT		
35**	11	1.1	105	-3.27	-2.15

\*\* Extreme Outlier or Excluded Result, see Section 4.2

**Statistics**

<b>Assigned Value</b>	21.6	4.8
<b>Spike Value</b>	21.0	1.0
<b>Robust Average</b>	21.6	4.8
<b>Median</b>	22.8	3.0
<b>Mean</b>	21.6	
<b>N</b>	10	
<b>Max</b>	29.19	
<b>Min</b>	13	
<b>Robust SD</b>	6.1	
<b>Robust CV</b>	28%	

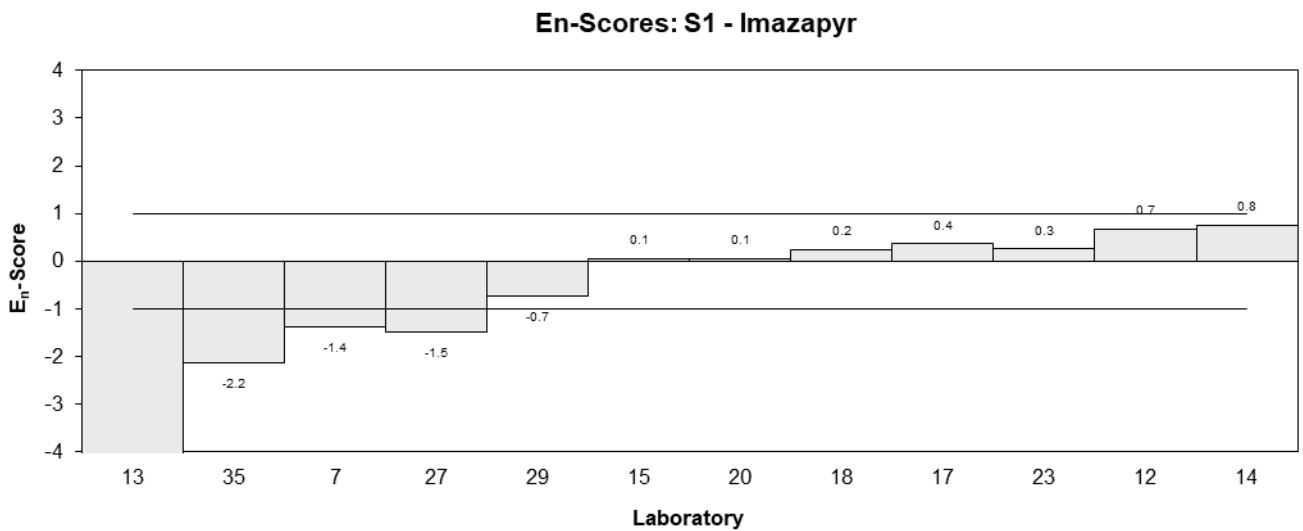
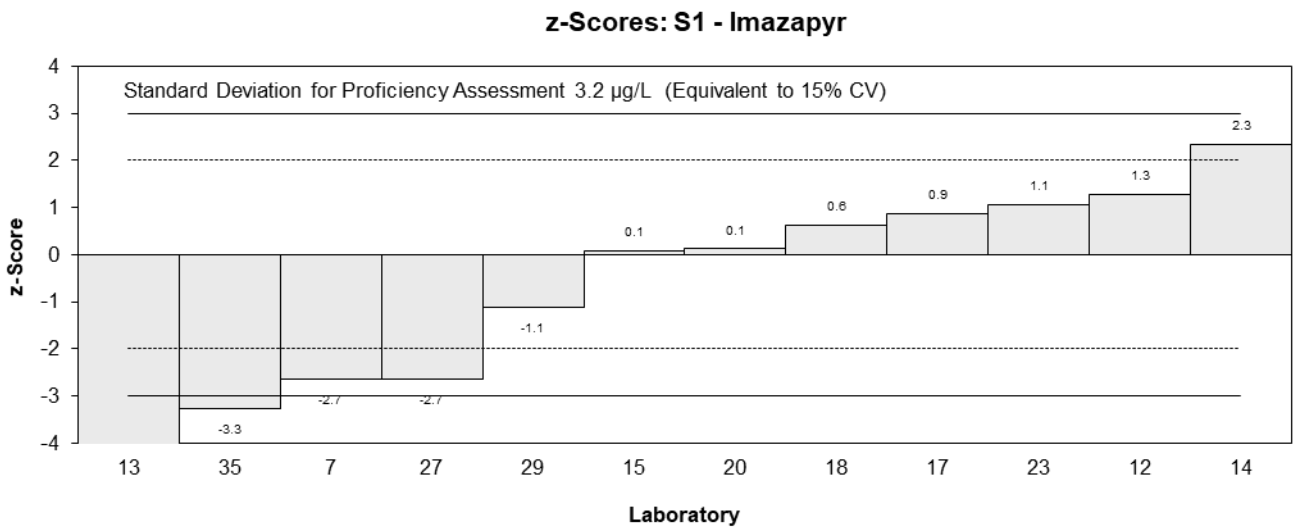
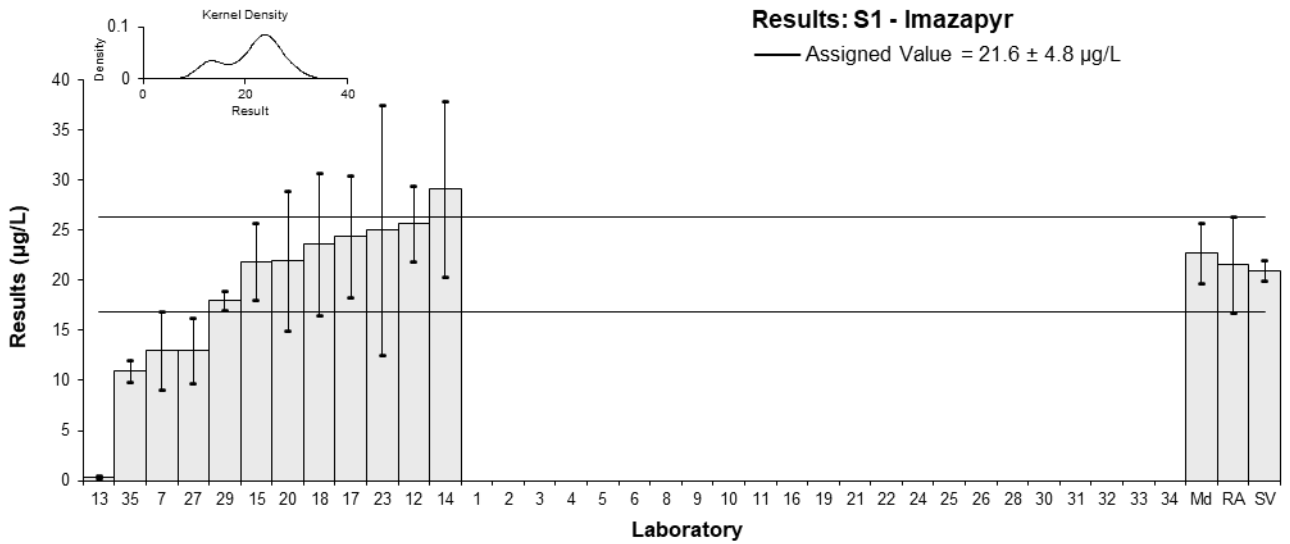


Figure 6

Table 11

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix</b>	River Water
<b>Analyte</b>	Metolachlor
<b>Unit</b>	µg/L

**Participant Results**

Lab. Code	Result	Uncertainty	Rec	z	E <sub>n</sub>
1	NT	NT	NT		
2	NT	NT	NT		
3	0.6	0.18	NR	1.74	0.67
4	0.4502	NT	94	-0.36	-0.55
5	0.432	0.11	NR	-0.62	-0.37
6	<1	NR	NR		
7	<0.01	NR	NR		
8	NS	NS	NS		
9	<2	NR	NR		
10	<0.01	NR	NR		
11	NT	NT	NT		
12*	0.13	0.04	NR	-4.85	-5.61
13	0.512	0.0736	52	0.50	0.41
14	< 0.2	NR	NR		
15	0.456	0.074	NR	-0.28	-0.23
16	NT	NT	NT		
17	0.49	0.12	95	0.20	0.11
18	0.42	0.13	NR	-0.78	-0.41
19	0.517	0.06	NR	0.57	0.54
20	<2	NR	NR		
21	NT	NT	NT		
22	0.475	0.097	NR	-0.01	-0.01
23	0.58	0.29	94	1.46	0.35
24	NT	NT	NT		
25	< 1	NR	NR		
26	NT	NT	NT		
27	<0.01	NR	NR		
28	0.52	0.10	NR	0.62	0.40
29	0.45	0.027	96	-0.36	-0.48
30	<2	NR	80-120		
31	NR	NR	NR		
32	0.4075	NT	94	-0.96	-1.46
33	0.3549	NT	94	-1.70	-2.58
34	NT	NT	NT		
35**	0.28	0.08	120	-2.75	-2.11

\* Outlier, \*\* Excluded Result, see Section 4.2

**Statistics**

<b>Assigned Value</b>	0.476	0.047
<b>Spike Value</b>	0.490	0.024
<b>Robust Average</b>	0.467	0.052
<b>Median</b>	0.456	0.046
<b>Mean</b>	0.453	
<b>N</b>	15	
<b>Max</b>	0.6	
<b>Min</b>	0.13	
<b>Robust SD</b>	0.080	
<b>Robust CV</b>	17%	

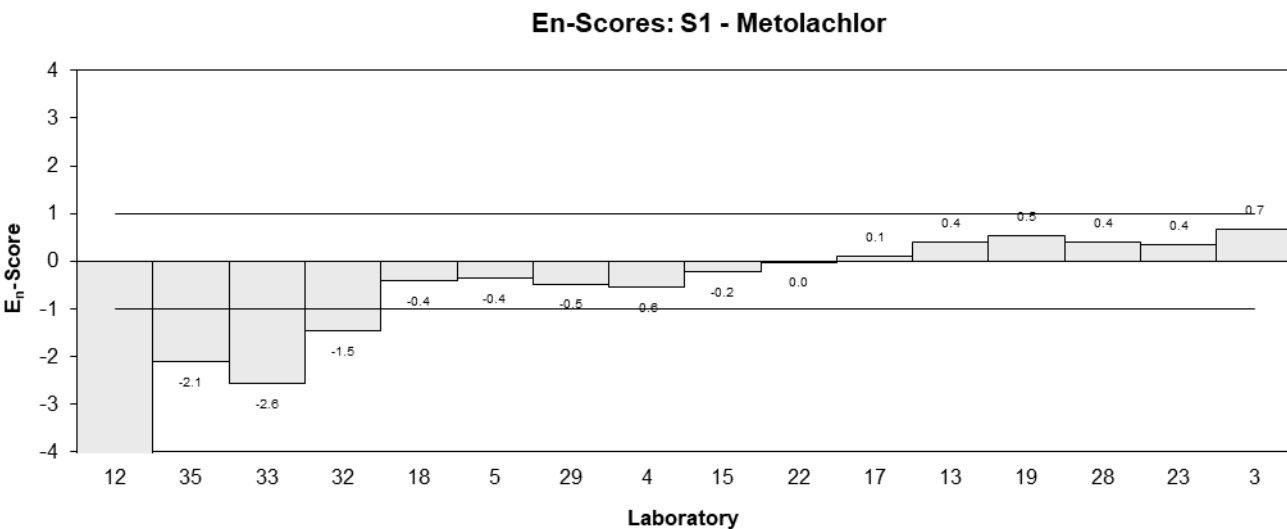
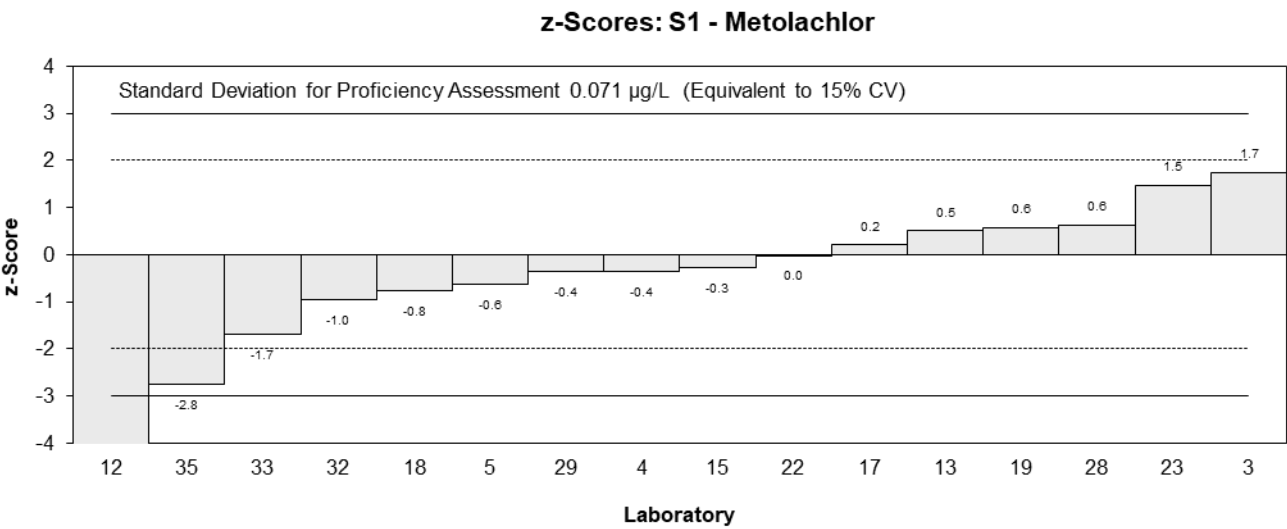
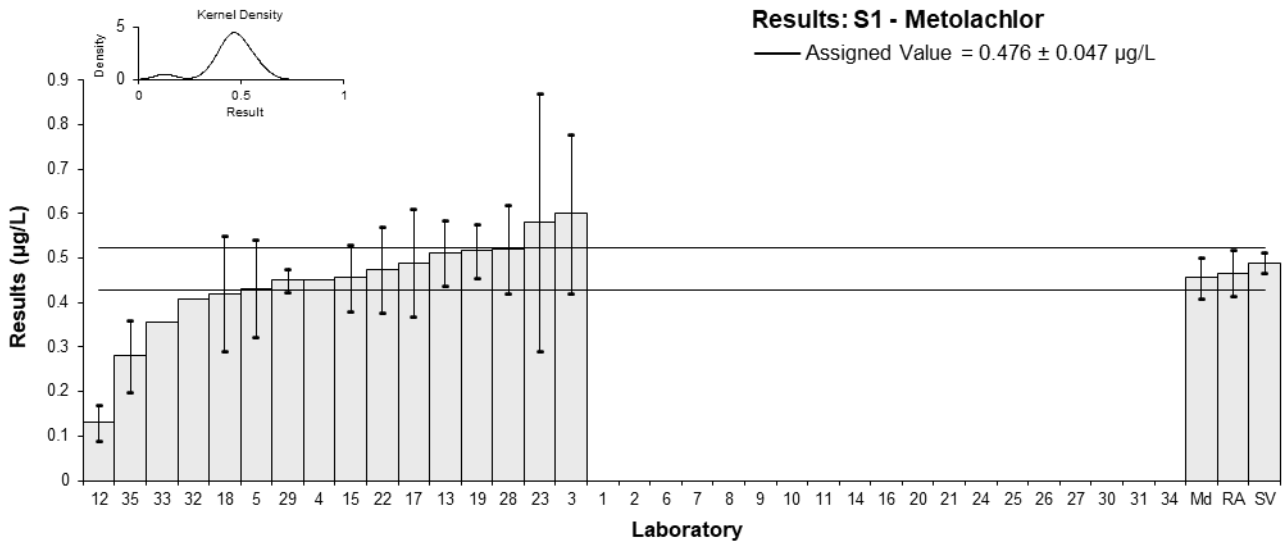


Figure 7

Table 12

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix</b>	River Water
<b>Analyte</b>	Atrazine
<b>Unit</b>	µg/L

**Participant Results**

Lab. Code	Result	Uncertainty	Rec	z	E <sub>n</sub>
1	2.4	0.6	96	0.74	0.39
2	1.4	0.93	NR	-2.35	-0.81
3	3.05	0.915	NR	2.75	0.96
4	2.295	NT	105	0.42	0.90
5	2.58	0.52	NR	1.30	0.78
6	2.31	0.19	103	0.46	0.62
7	2	0.6	91	-0.49	-0.26
8	NS	NS	NS		
9	2	1	NR	-0.49	-0.16
10	2.34	0.23	NR	0.56	0.66
11	NT	NT	NT		
12*	0.85	0.25	NR	-4.04	-4.49
13	2.49	0.393	63	1.02	0.78
14	2.3	0.69	NR	0.43	0.20
15	2.15	0.370	NR	-0.03	-0.03
16	2.5	0.75	70	1.05	0.44
17	2.27	0.57	86	0.34	0.19
18	2.16	0.52	NR	0.00	0.00
19	1.94	0.5	NR	-0.68	-0.42
20	2.2	0.7	NR	0.12	0.06
21	2.3	0.28	NR	0.43	0.44
22	1.57	0.76	NR	-1.82	-0.76
23	2.9	1.45	98	2.28	0.51
24	NT	NT	NT		
25	1.9	0.57	NR	-0.80	-0.44
26	2.06	0.46	NR	-0.31	-0.21
27	1.6	0.4	91	-1.73	-1.31
28	2.2	0.44	NR	0.12	0.09
29	1.9	0.17	117	-0.80	-1.15
30	2	1	80-120	-0.49	-0.16
31	NR	NR	NR		
32	1.9296	NT	114	-0.71	-1.54
33	1.9322	NT	105	-0.70	-1.52
34	NT	NT	NT		
35**	1.3	0.3	110	-2.65	-2.56

\* Outlier, \*\* Excluded Result, see Section 4.2

**Statistics**

<b>Assigned Value</b>	2.16	0.15
<b>Spike Value</b>	2.49	0.12
<b>Robust Average</b>	2.14	0.16
<b>Median</b>	2.16	0.15
<b>Mean</b>	2.12	
<b>N</b>	29	
<b>Max</b>	3.05	
<b>Min</b>	0.85	
<b>Robust SD</b>	0.35	
<b>Robust CV</b>	16%	

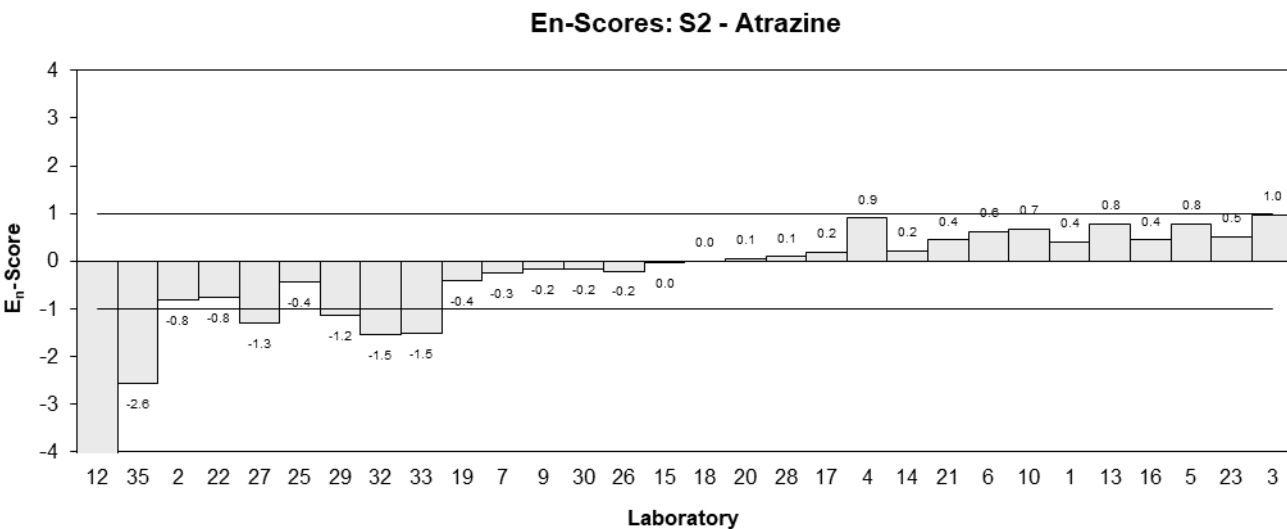
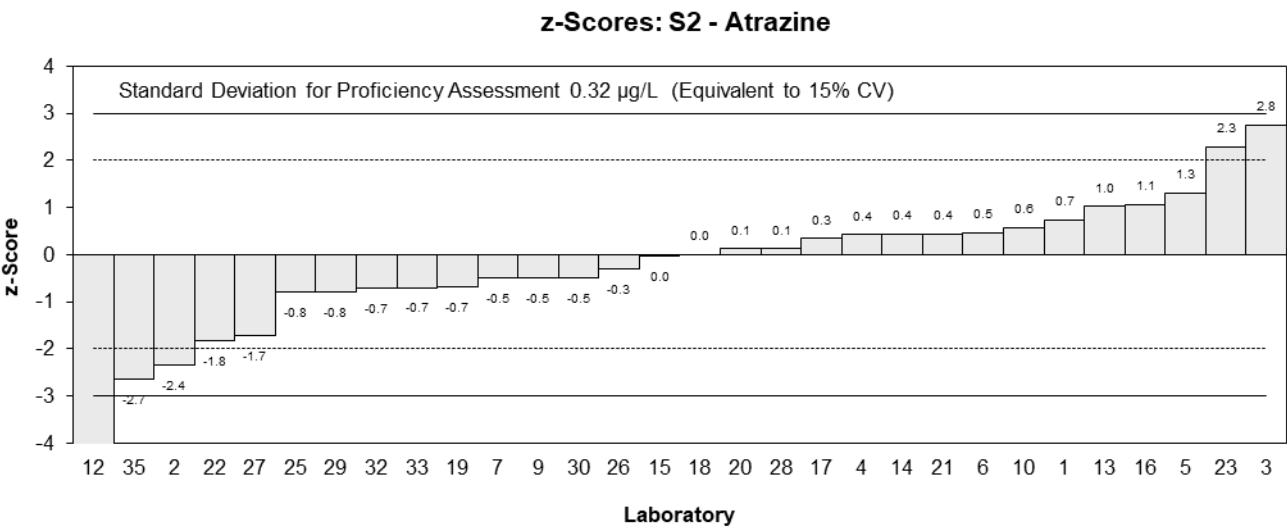
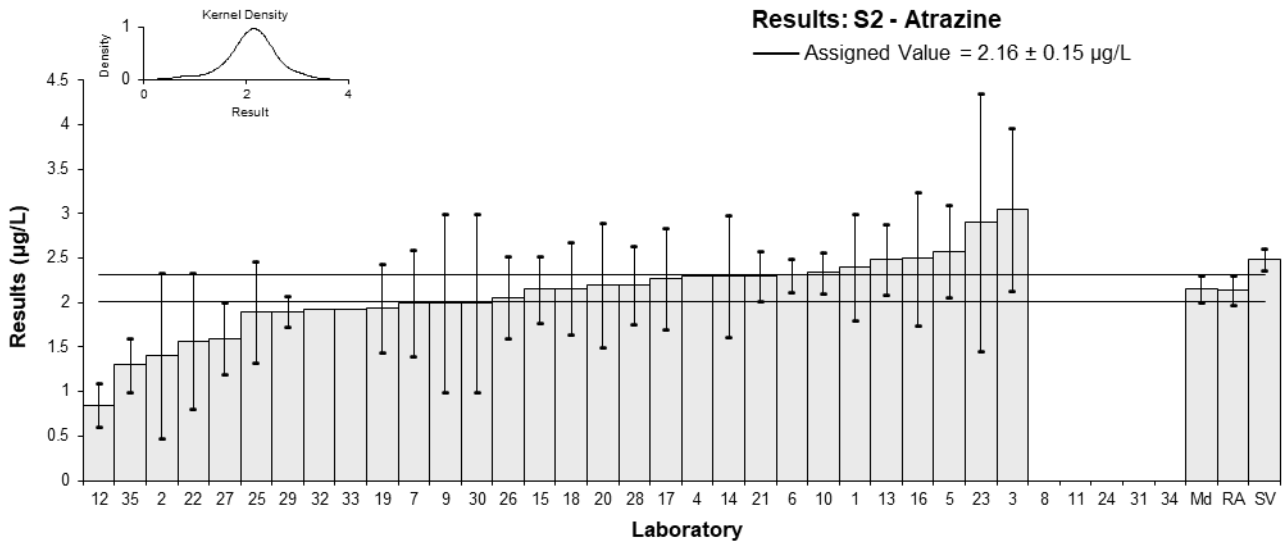


Figure 8

Table 13

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix</b>	River Water
<b>Analyte</b>	Deltamethrin
<b>Unit</b>	µg/L

**Participant Results**

Lab. Code	Result	Uncertainty	Rec
1	NT	NT	NT
2	NT	NT	NT
3	0.79	0.237	NR
4	NT	NT	NT
5	5.823	1.46	NR
6	1.97	1.24	114
7**	0.21	0.063	86
8	NS	NS	NS
9	4	2	NR
10	NT	NT	NT
11	NT	NT	NT
12	3.58	1.07	NR
13	NT	NT	NT
14	< 0.05	NR	NR
15	NT	NT	NT
16	1.92	0.58	108
17	NT	NT	NT
18	3.69	1.07	NR
19	7.64	2	NR
20	3.8	1	NR
21	NT	NT	NT
22	4.5	1.6	NR
23	3.8	1.9	90
24	NT	NT	NT
25	NT	NT	NT
26	NT	NT	NT
27	2.8	0.7	86
28	2.1	0.42	NR
29	1.6	0.14	86
30	6.3	3	80-120
31	NR	NR	NR
32	NT	NT	NT
33	NT	NT	NT
34	NT	NT	NT
35	NT	NT	NT

\*\* Extreme Outlier, see Section 4.2

**Statistics**

<b>Assigned Value</b>	Not Set	
<b>Spike Value</b>	19.1	1.0
<b>Robust Average</b>	3.5	1.3
<b>Median</b>	3.7	1.5
<b>Mean</b>	3.62	
<b>N</b>	15	
<b>Max</b>	7.64	
<b>Min</b>	0.79	
<b>Robust SD</b>	2.0	
<b>Robust CV</b>	55%	

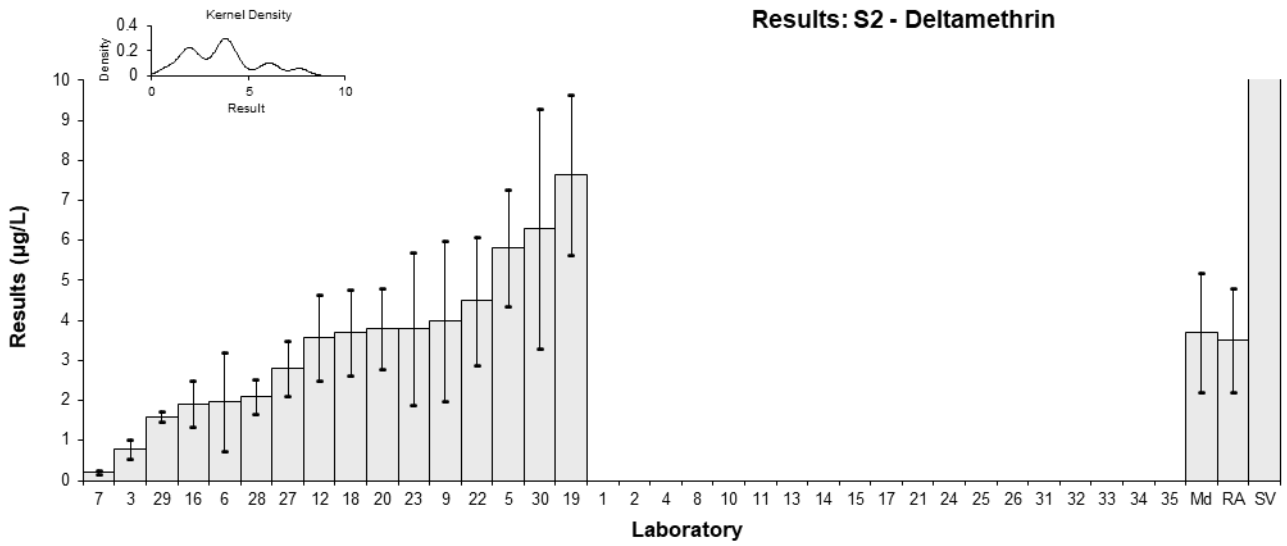


Figure 9

Table 14

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix</b>	River Water
<b>Analyte</b>	Diazinon
<b>Unit</b>	µg/L

**Participant Results**

Lab. Code	Result	Uncertainty	Rec	z	E <sub>n</sub>
1	<0.5	NR	96		
2	< 0.5	0.36	NR		
3*	0.34	0.102	NR	4.28	1.26
4*	0.1014	NT	107	-3.40	-3.91
5	0.23	0.053	NR	0.74	0.39
6	<1	NR	NR		
7	0.2	0.06	94	-0.23	-0.11
8	NS	NS	NS		
9	<0.2	NR	NR		
10	0.24	0.03	NR	1.06	0.82
11	< 2	NR	NR		
12	<0.01	NR	NR		
13	0.293	0.00953	44	2.77	3.00
14	< 0.1	NR	NR		
15	0.18	0.030	NR	-0.87	-0.67
16	<0.5	0.5	NR		
17	0.20	0.05	95	-0.23	-0.12
18	0.19	0.06	NR	-0.55	-0.26
19	0.241	0.08	NR	1.10	0.40
20	<0.2	NR	NR		
21	0.2	0.024	NR	-0.23	-0.19
22	0.21	0.06	NR	0.10	0.05
23	0.27	0.14	87	2.03	0.44
24	NT	NT	NT		
25	< 2	NR	NR		
26	<0.5	NR	NR		
27	0.21	0.0525	94	0.10	0.05
28	0.24	0.048	NR	1.06	0.60
29	0.16	0.012	72	-1.51	-1.59
30	<0.2	NR	80-120		
31	<2	NR	NR		
32	0.1074	NT	108	-3.21	-3.69
33	0.1076	NT	107	-3.20	-3.68
34	0.2	0.06	80	-0.23	-0.11
35**	0.1	0.03	85	-3.45	-2.65

\* Outlier, \*\* Excluded Result, see Section 4.2

**Statistics**

<b>Assigned Value</b>	0.207	0.027
<b>Spike Value</b>	0.251	0.013
<b>Robust Average</b>	0.205	0.036
<b>Median</b>	0.200	0.034
<b>Mean</b>	0.206	
<b>N</b>	19	
<b>Max</b>	0.34	
<b>Min</b>	0.1014	
<b>Robust SD</b>	0.062	
<b>Robust CV</b>	30%	

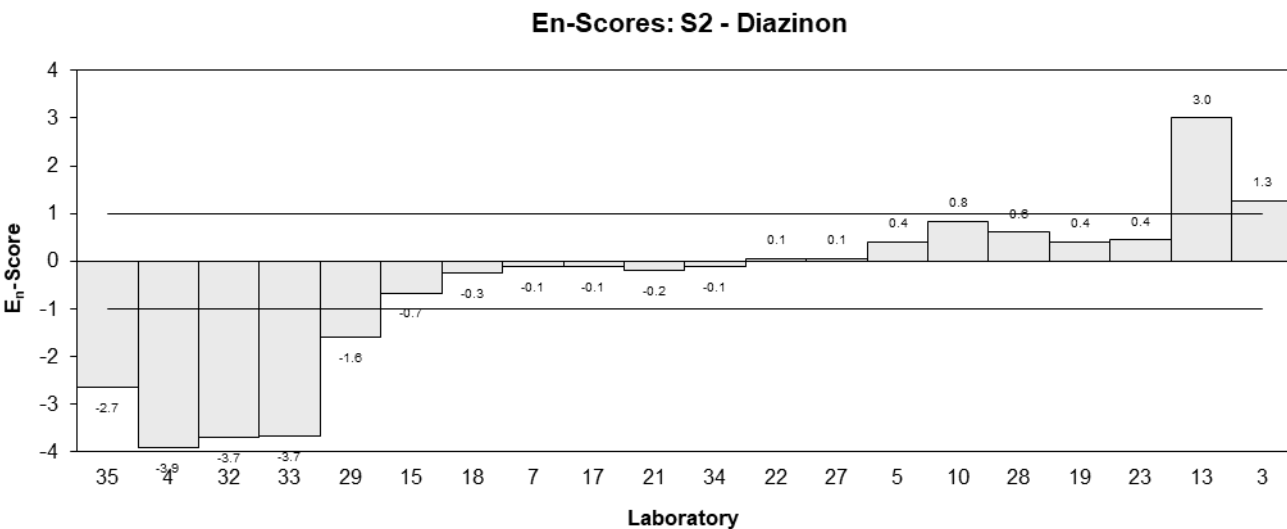
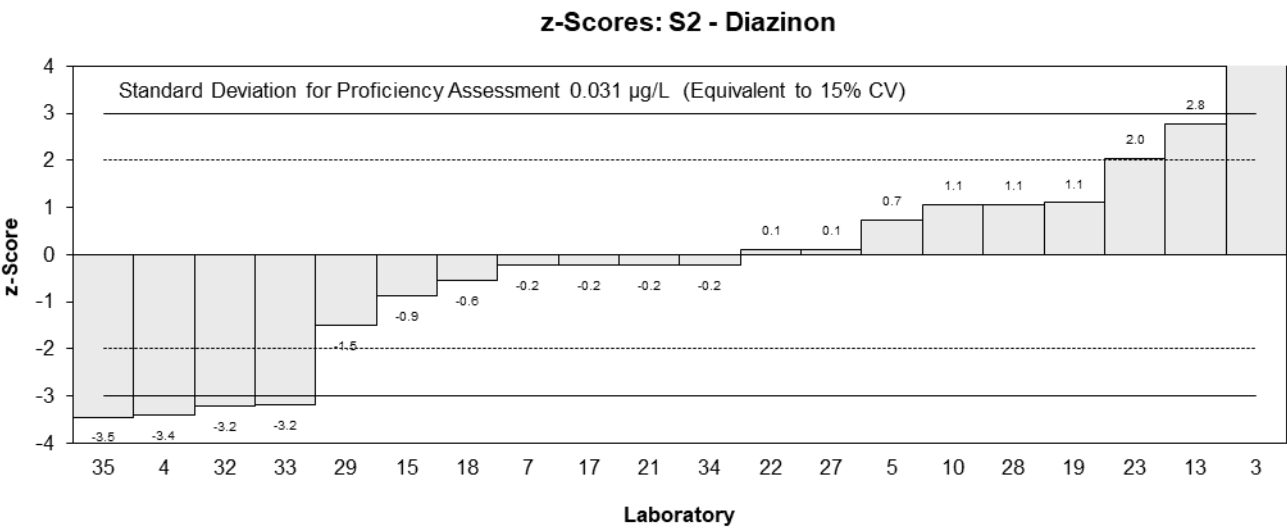
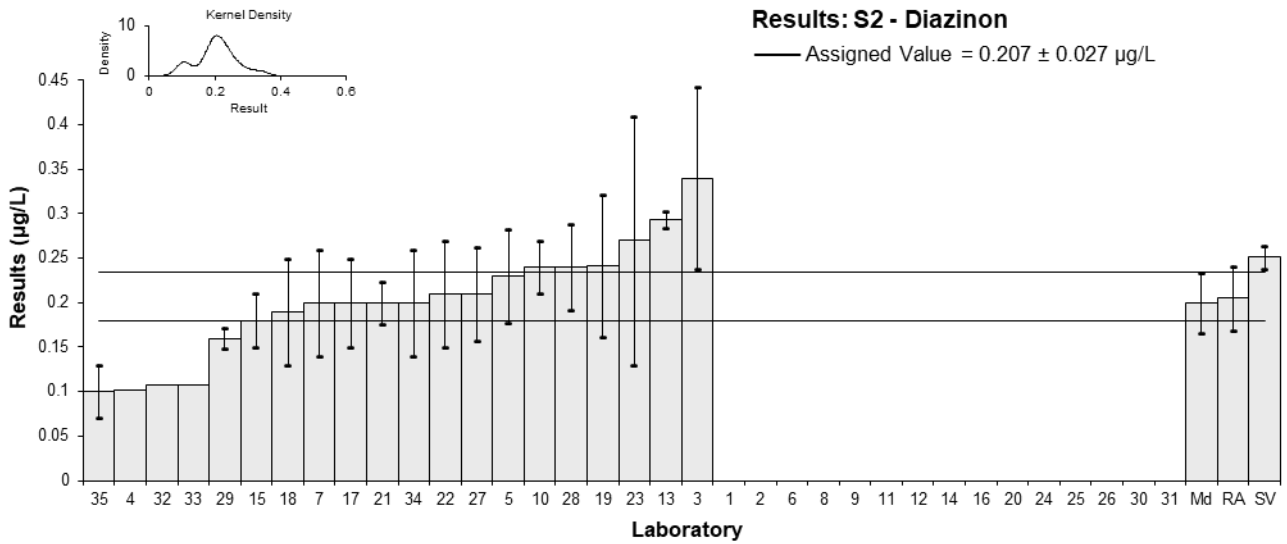


Figure 10

Table 15

## Sample Details

Sample No.	S2
Matrix	River Water
Analyte	Dimethoate
Unit	µg/L

## Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E <sub>n</sub>
1	9.7	3.3	96	0.36	0.15
2	7.3	6.43	NR	-1.38	-0.29
3*	15.5	4.65	NR	2.00▼	
4	10.3717	NT	107	0.85	1.17
5	13.3	3.33	NR	2.00▼	
6	7.83	0.97	96	-0.99	-0.98
7	7.9	2.37	102	-0.94	-0.51
8	NS	NS	NS		
9	11	3	NR	1.30	0.57
10	8.25	1.24	NR	-0.69	-0.60
11	6.64	1.992	NR	-1.86	-1.15
12*	3.77	1.1	NR	-3.93	-3.65
13	NT	NT	NT		
14	6.58	1.97	NR	-1.90	-1.19
15*	14.7	2.751	NR	2.00▼	
16	12.8	3.8	99	2.00▼	
17	13.95	3.49	88	2.00▼	
18	9.24	2.68	NR	0.03	0.01
19	10.1	1.3	NR	0.65	0.55
20	9.1	3	NR	-0.07	-0.03
21	NT	NT	NT		
22	8.8	5.3	NR	-0.29	-0.07
23	8.9	4.45	91	-0.22	-0.07
24	NT	NT	NT		
25	6.5	1.95	NR	-1.96	-1.23
26	9.40	2.46	NR	0.14	0.08
27	9.1	2.275	102	-0.07	-0.04
28	8.4	1.7	NR	-0.58	-0.41
29	11	0.32	97	1.30	1.71
30	8.9	3	80-120	-0.22	-0.09
31*	19	5.7	124	2.00▼	
32	8.726	NT	101	-0.34	-0.47
33	4.9502	NT	107	-3.08	-4.25
34	11.54	3.5	70	1.70	0.64
35**	7.3	1.5	110	-1.38	-1.05

\* Outlier, \*\* Excluded Result, see Section 4.2; ▼ Adjusted Score, see Section 6.3

## Statistics

Assigned Value	9.2	1.0
Spike Value	16.9	0.8
Robust Average	9.6	1.3
Max Acceptable Result	22.0	
Median	9.1	1.0
Mean	9.8	
N	30	
Max	19	
Min	3.77	
Robust SD	2.9	
Robust CV	30%	

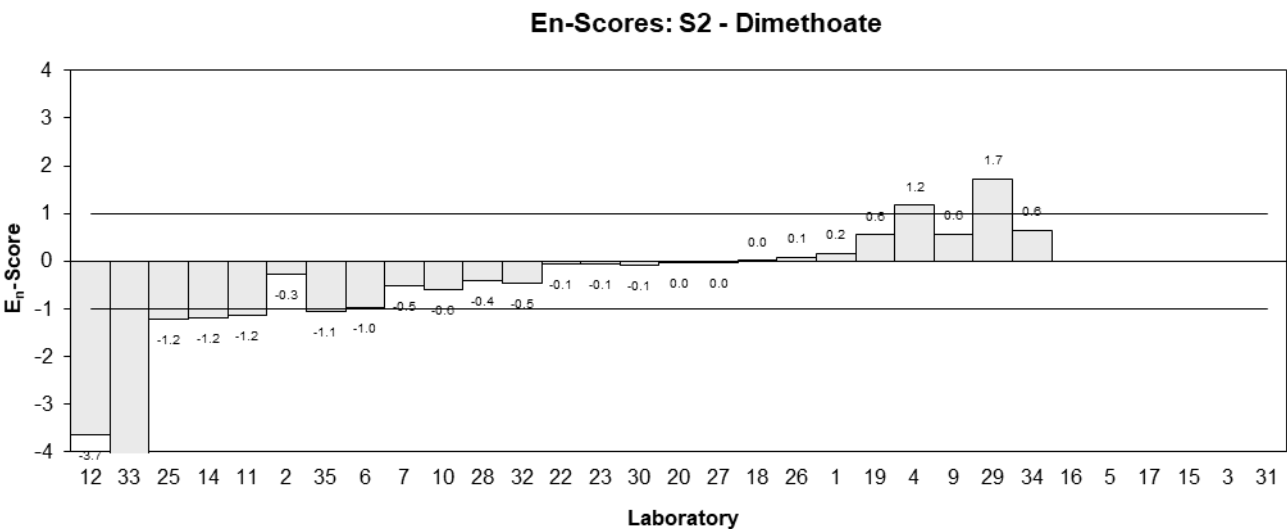
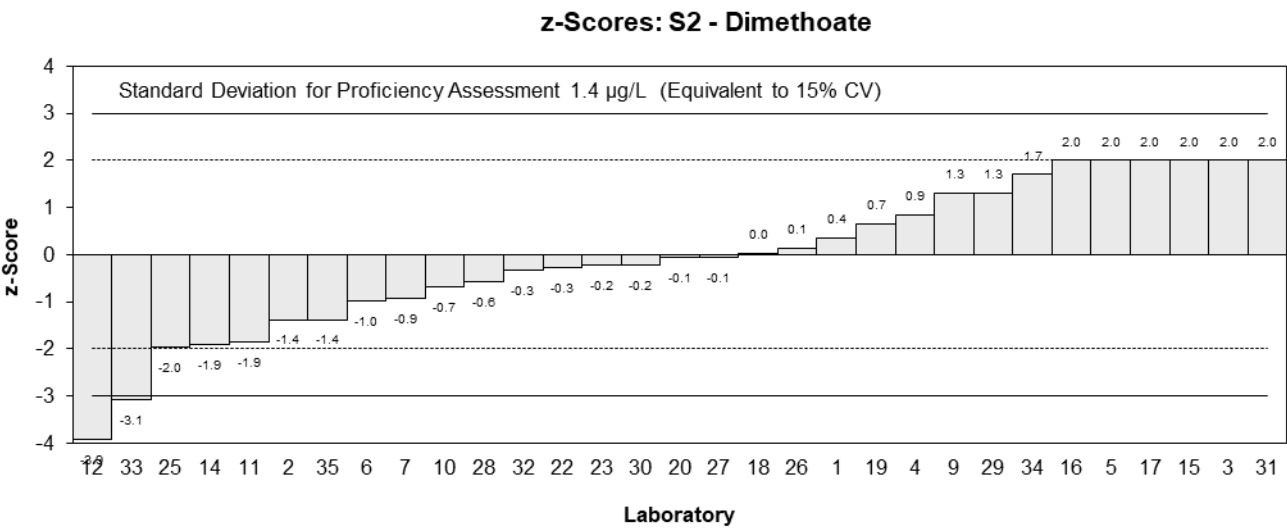
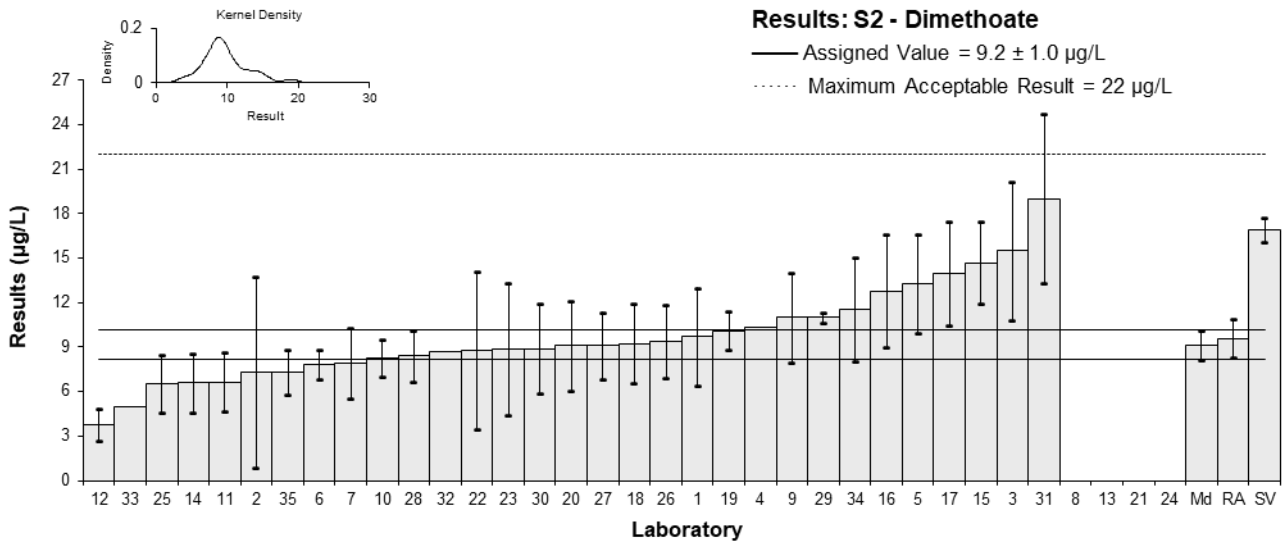


Figure 11

Table 16

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix</b>	River Water
<b>Analyte</b>	Fenthion
<b>Unit</b>	µg/L

**Participant Results**

Lab. Code	Result	Uncertainty	Rec	z	E <sub>n</sub>
1	2.8	0.7	96	0.25	0.14
2	1.8	1.35	NR	-2.22	-0.66
3	NT	NT	NT		
4	NT	NT	NT		
5	2.61	0.52	NR	-0.22	-0.16
6	NT	NT	NT		
7	2.16	0.648	116	-1.33	-0.79
8	NS	NS	NS		
9	2.8	1.1	NR	0.25	0.09
10	3.1	0.68	NR	0.99	0.56
11	2.2	0.66	NR	-1.23	-0.72
12*	0.7	0.2	NR	-4.94	-6.56
13*	4.1	0.144	21	3.46	5.16
14	2.98	0.89	NR	0.69	0.30
15	2.72	0.340	NR	0.05	0.05
16	2.84	0.85	116	0.35	0.16
17	NT	NT	NT		
18	NT	NT	NT		
19	3.13	0.8	NR	1.06	0.52
20	2.7	0.8	NR	0.00	0.00
21	NT	NT	NT		
22	NT	NT	NT		
23	3.1	1.55	97	0.99	0.26
24	NT	NT	NT		
25	2.7	0.81	NR	0.00	0.00
26	3.37	0.77	NR	1.65	0.83
27	2.2	0.55	116	-1.23	-0.84
28	2.5	0.49	NR	-0.49	-0.37
29	2.3	0.13	92	-0.99	-1.51
30	2.8	0.8	80-120	0.25	0.12
31	2.9	0.87	124	0.49	0.22
32	NT	NT	NT		
33	NT	NT	NT		
34	NT	NT	NT		
35	NT	NT	NT		

\* Outlier, see Section 4.2

**Statistics**

<b>Assigned Value</b>	2.70	0.23
<b>Spike Value</b>	3.02	0.15
<b>Robust Average</b>	2.69	0.25
<b>Median</b>	2.76	0.24
<b>Mean</b>	2.66	
<b>N</b>	22	
<b>Max</b>	4.1	
<b>Min</b>	0.7	
<b>Robust SD</b>	0.47	
<b>Robust CV</b>	17%	

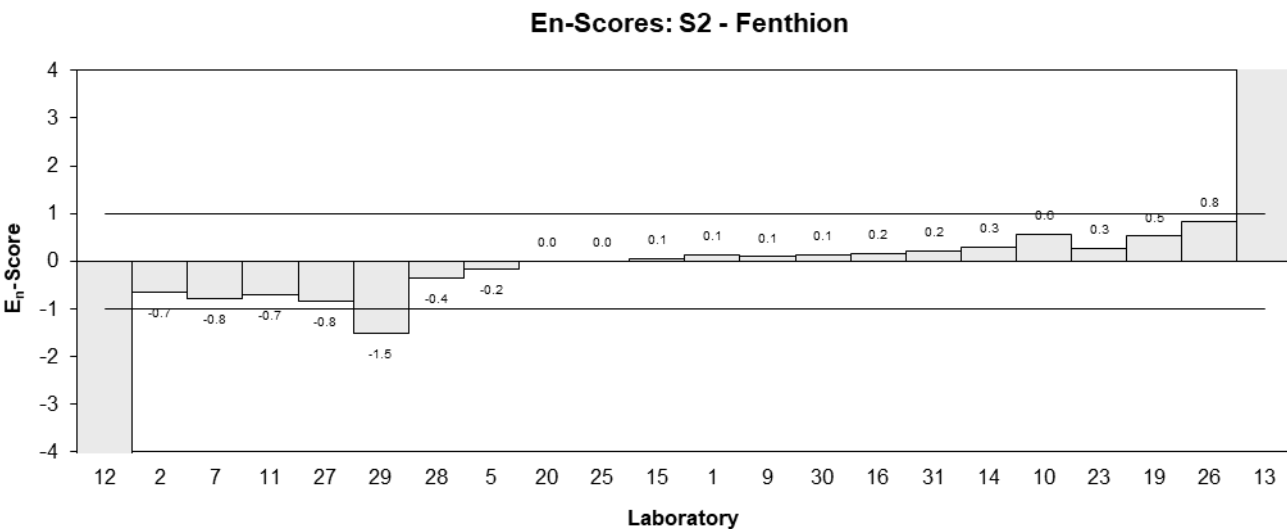
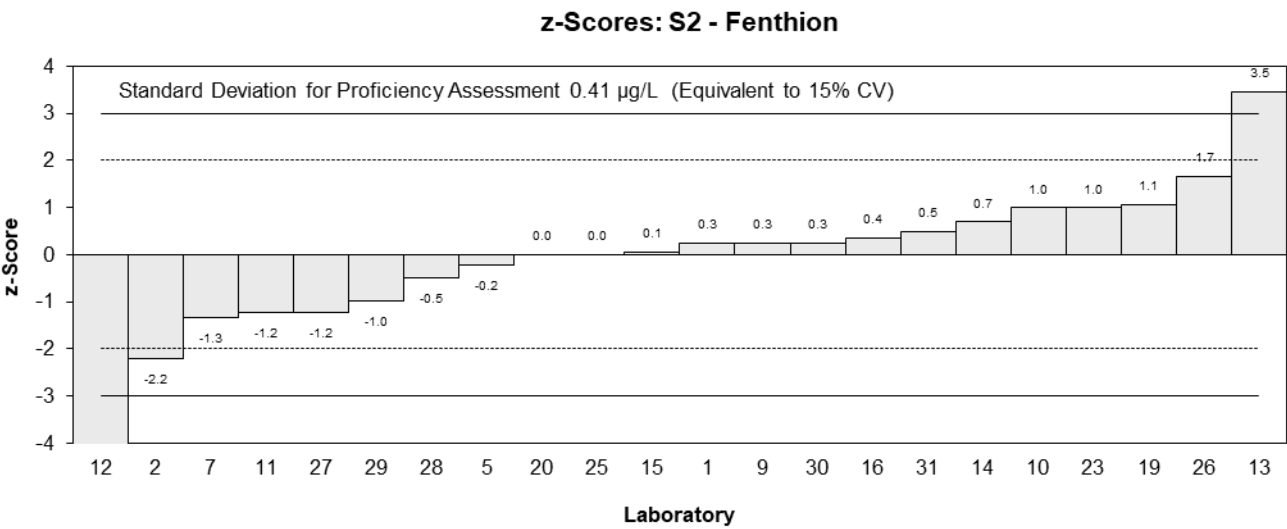
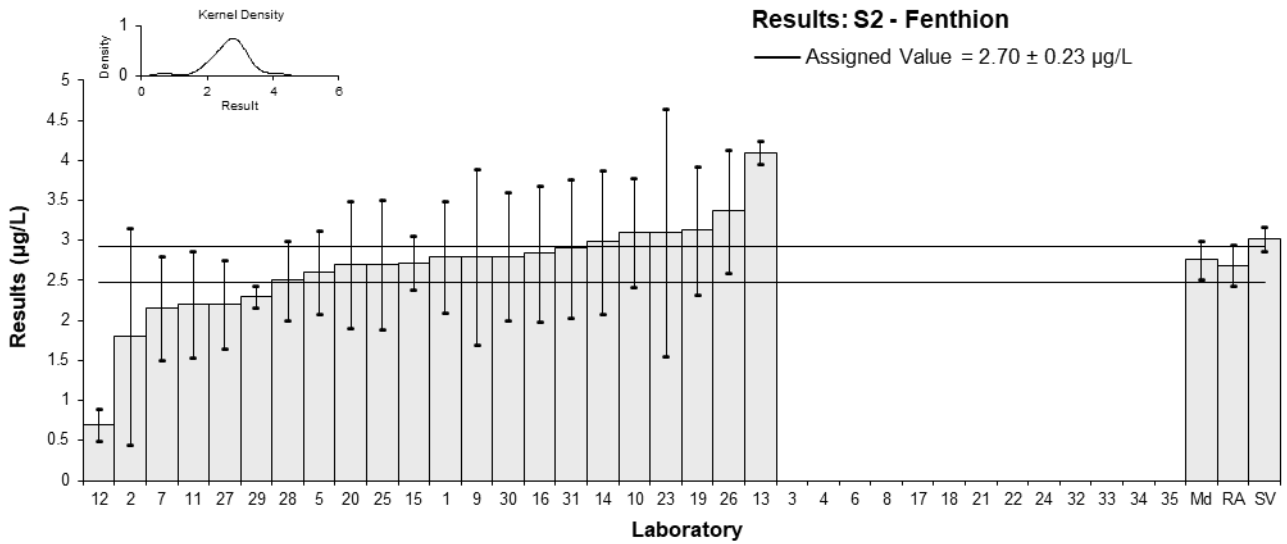


Figure 12

Table 17

## Sample Details

<b>Sample No.</b>	S2
<b>Matrix</b>	River Water
<b>Analyte</b>	Metsulfuron-methyl
<b>Unit</b>	µg/L

## Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E <sub>n</sub>
1	NT	NT	NT		
2	NT	NT	NT		
3	NT	NT	NT		
4	NT	NT	NT		
5	NT	NT	NT		
6	NT	NT	NT		
7	3.1	0.93	50	-0.78	-0.38
8	NS	NS	NS		
9	NT	NT	NT		
10	4.43	1.24	NR	1.75	0.68
11	NT	NT	NT		
12	3.6	0.5	97	0.17	0.12
13	3.17	0.657	88	-0.65	-0.41
14	< 2.5	NR	NR		
15*	1.46	NR	NR	-3.89	-3.94
16	NT	NT	NT		
17	3.30	0.83	81	-0.40	-0.21
18	3.49	1.05	NR	-0.04	-0.02
19	NT	NT	NT		
20	3.2	1	NR	-0.59	-0.28
21	4.04	0.848	NR	1.01	0.53
22	NT	NT	NT		
23	4.2	2.1	99	1.31	0.32
24	NT	NT	NT		
25	< 10	NR	NR		
26	NT	NT	NT		
27*	10	2.5	24	12.33	2.54
28	NT	NT	NT		
29	2.3	0.36	78	-2.30	-1.91
30	NT	NT	NT		
31	NR	NR	NR		
32	NT	NT	NT		
33	NT	NT	NT		
34	NT	NT	NT		
35**	1.7	0.51	80	-3.44	-2.49

\* Outlier, \*\* Excluded Result, see Section 4.2

## Statistics

<b>Assigned Value</b>	3.51	0.52
<b>Spike Value</b>	3.52	0.18
<b>Robust Average</b>	3.48	0.67
<b>Median</b>	3.40	0.50
<b>Mean</b>	3.9	
<b>N</b>	12	
<b>Max</b>	10	
<b>Min</b>	1.46	
<b>Robust SD</b>	0.93	
<b>Robust CV</b>	27%	

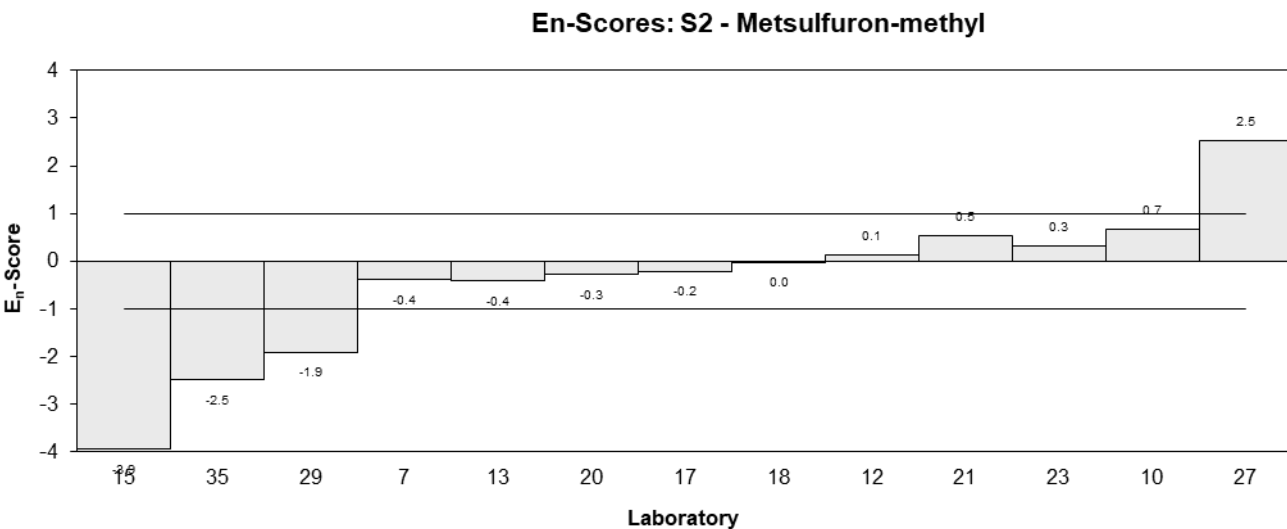
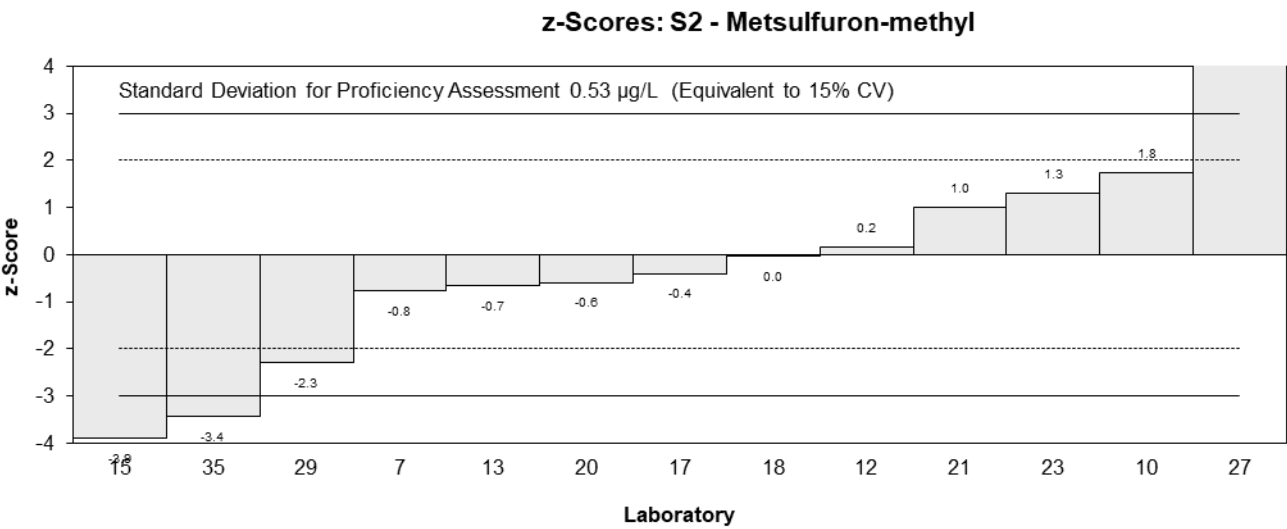
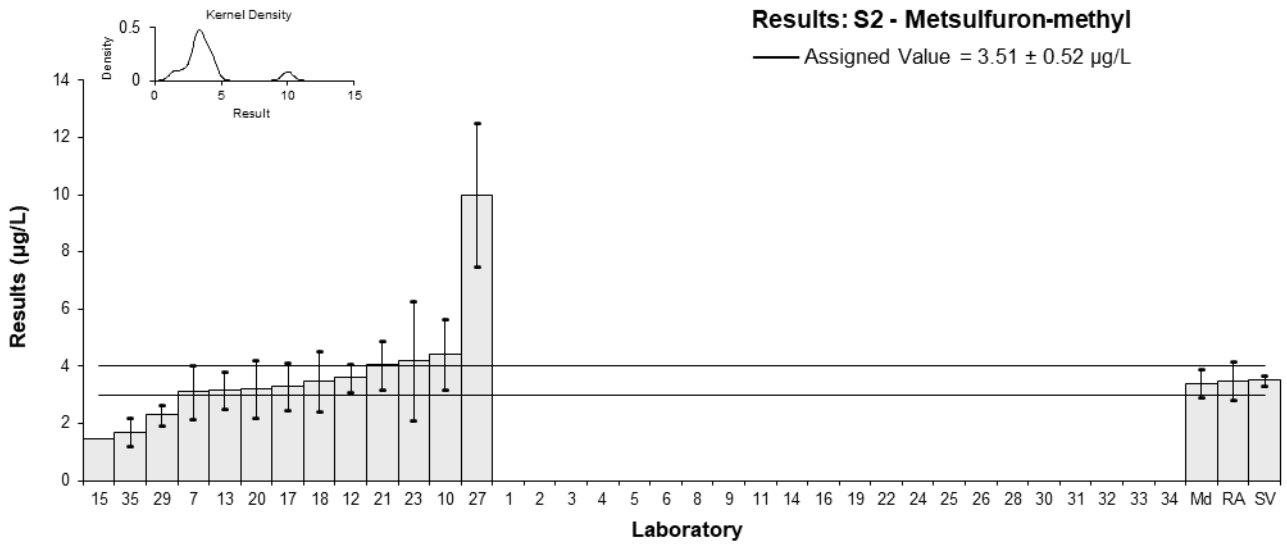


Figure 13

Table 18

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix</b>	River Water
<b>Analyte</b>	AMPA
<b>Unit</b>	µg/L

**Participant Results**

Lab. Code	Result	Uncertainty	Rec	z	E <sub>n</sub>
1	6.5	0.8	117	-0.81	-0.66
2	NT	NT	NT		
3	NT	NT	NT		
4	NS	NS	NS		
5	<30	NR	NR		
6	NT	NT	NT		
7	NT	NT	NT		
8	6.82	0.88	111	-0.52	-0.41
9	NT	NT	NT		
10	7.71	1.54	NR	0.28	0.16
11	NS	NS	NS		
12**	19	5.7	NR	10.45	2.00
13	NT	NT	NT		
14	10.49	3.1	109	2.78	0.94
15	5.52	1.650	NR	-1.69	-0.95
16	NT	NT	NT		
17	NT	NT	NT		
18	6.96	2.16	92	-0.40	-0.18
19	NT	NT	NT		
20	<20	NR	NR		
21	7.3	1.13	NR	-0.09	-0.06
22	NT	NT	NT		
23	7	3.5	99	-0.36	-0.11
24	NT	NT	NT		
25	NS	NS	NS		
26	NS	NS	NS		
27	NT	NT	NT		
28	7.0	1.4	NR	-0.36	-0.22
29	NT	NT	NT		
30	NT	NT	NT		
31	10	3	99	2.34	0.81
32	NS	NS	NS		
33	NS	NS	NS		
34	NS	NS	NS		
35	NS	NS	NS		

\*\* Excluded Result, see Section 4.2

**Statistics**

<b>Assigned Value</b>	7.4	1.1
<b>Spike Value</b>	7.11	0.36
<b>Robust Average</b>	7.4	1.1
<b>Median</b>	7.00	0.47
<b>Mean</b>	7.53	
<b>N</b>	10	
<b>Max</b>	10.49	
<b>Min</b>	5.52	
<b>Robust SD</b>	1.4	
<b>Robust CV</b>	19%	

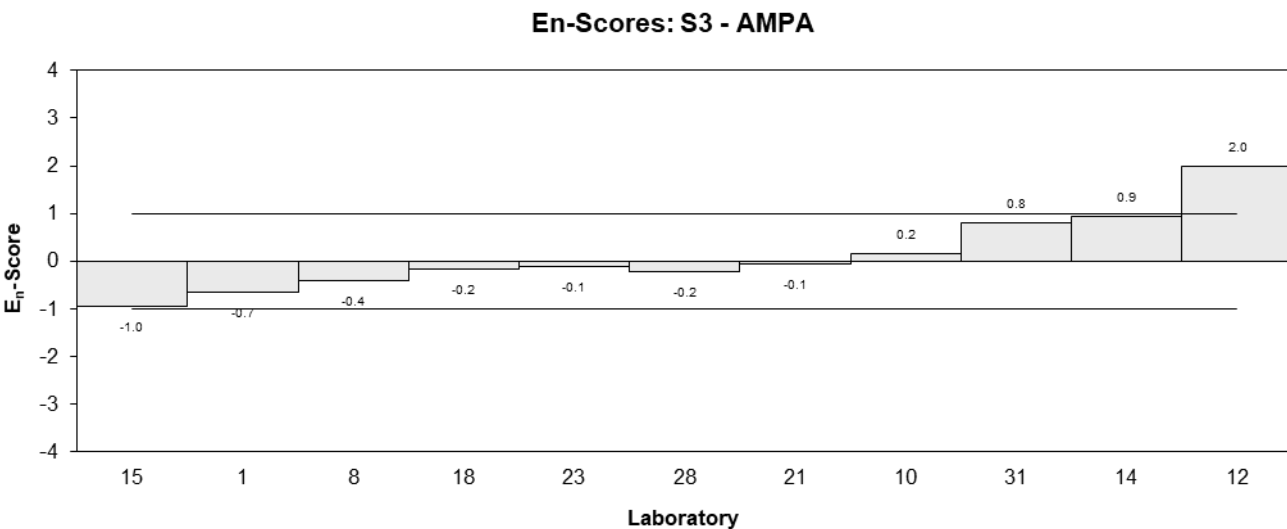
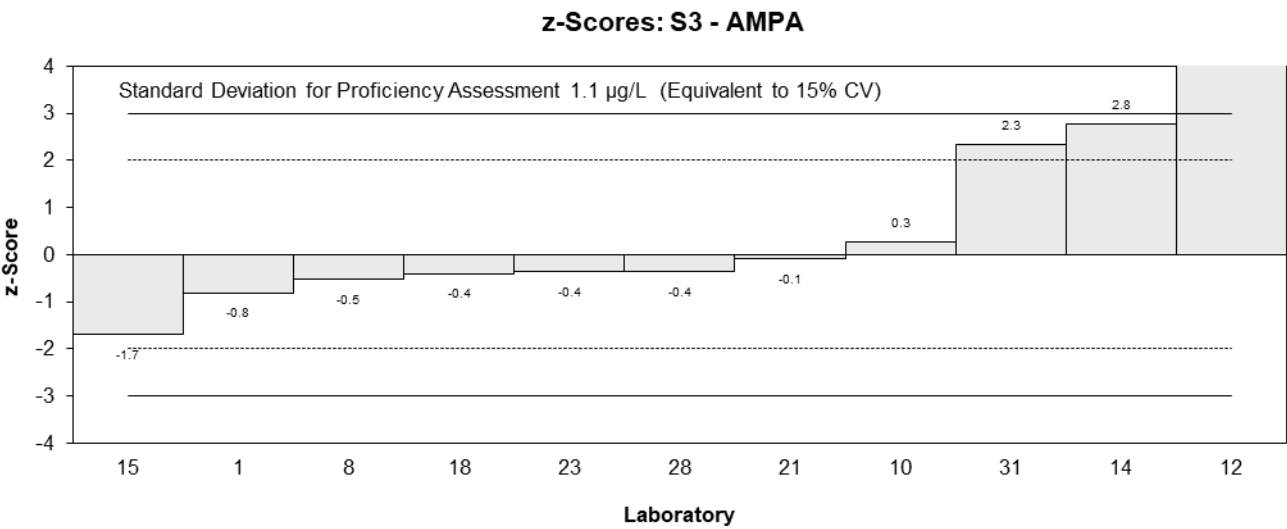
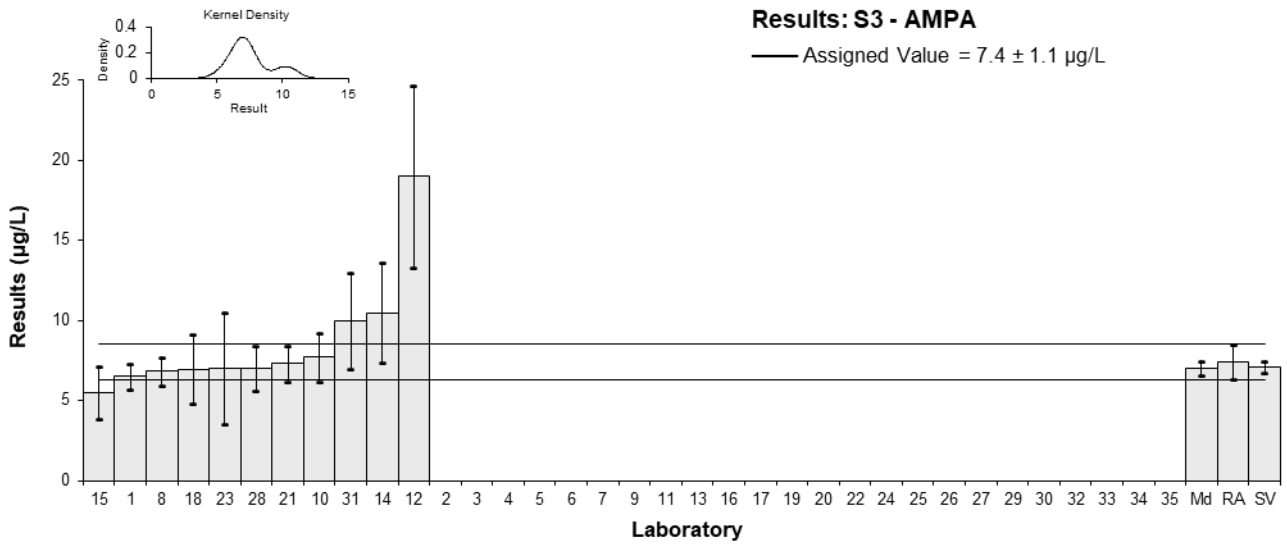


Figure 14

Table 19

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix</b>	River Water
<b>Analyte</b>	Glyphosate
<b>Unit</b>	µg/L

**Participant Results**

Lab. Code	Result	Uncertainty	Rec	z	E <sub>n</sub>
1	2.7	0.5	125	-0.78	-0.64
2	NT	NT	NT		
3	NT	NT	NT		
4	NS	NS	NS		
5	<30	NR	NR		
6	<10	NR	NR		
7	NT	NT	NT		
8	3.29	0.37	102	0.50	0.51
9	NT	NT	NT		
10	3.1	0.59	NR	0.09	0.06
11	NS	NS	NS		
12**	8	2.9	94	10.76	1.70
13	3.165	0.064	133	0.23	0.39
14*	5.55	1.7	103	5.42	1.45
15	2.64	0.900	NR	-0.92	-0.45
16	NT	NT	NT		
17	NT	NT	NT		
18	3.31	1	105	0.54	0.24
19	2.75	0.8	NR	-0.68	-0.37
20	<10	NR	NR		
21	3.5	0.68	NR	0.96	0.60
22	NT	NT	NT		
23	3	1.5	102	-0.13	-0.04
24	NT	NT	NT		
25	NS	NS	NS		
26	NS	NS	NS		
27	NT	NT	NT		
28	3.1	0.60	NR	0.09	0.06
29	NT	NT	NT		
30	NT	NT	NT		
31	<10	NR	NR		
32	NS	NS	NS		
33	NS	NS	NS		
34	NS	NS	NS		
35	NS	NS	NS		

\* Outlier, \*\* Excluded Result, see Section 4.2

**Statistics**

<b>Assigned Value</b>	3.06	0.26
<b>Spike Value</b>	3.00	0.15
<b>Robust Average</b>	3.11	0.28
<b>Median</b>	3.10	0.23
<b>Mean</b>	3.28	
<b>N</b>	11	
<b>Max</b>	5.55	
<b>Min</b>	2.64	
<b>Robust SD</b>	0.37	
<b>Robust CV</b>	12%	

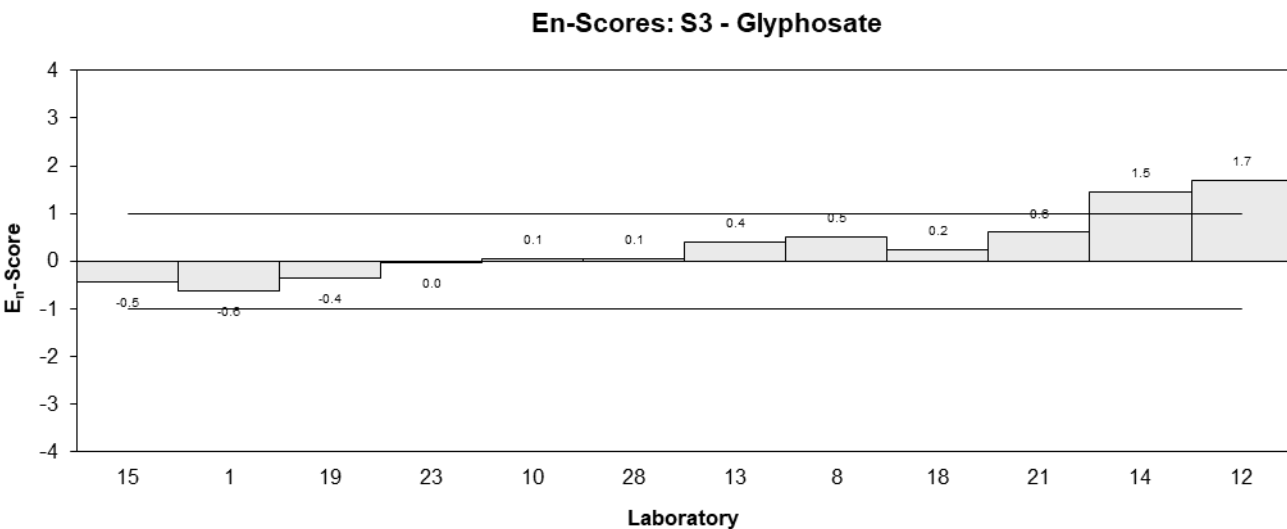
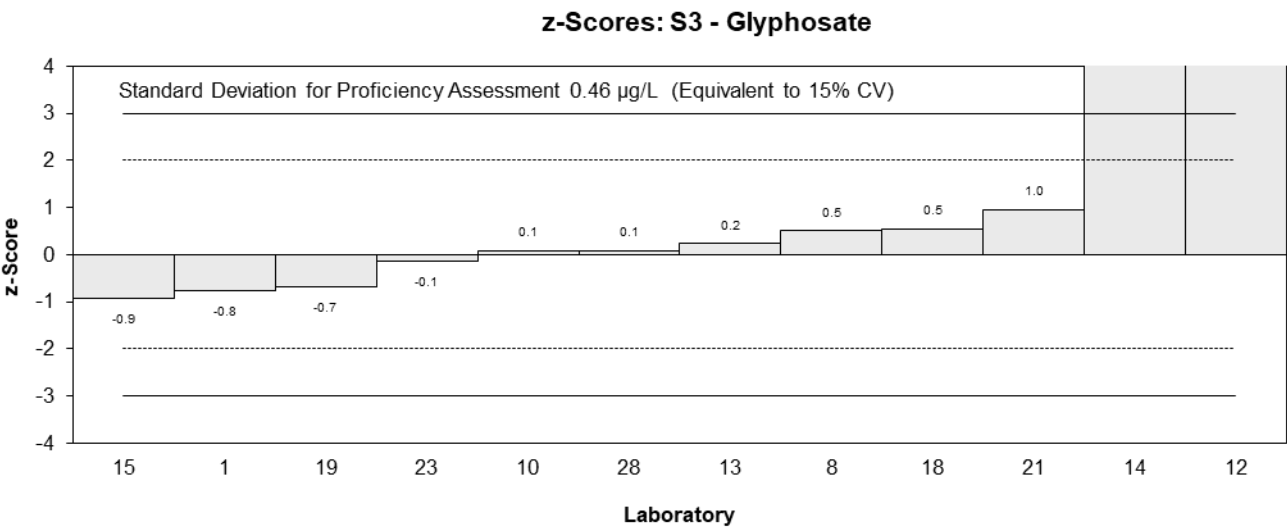
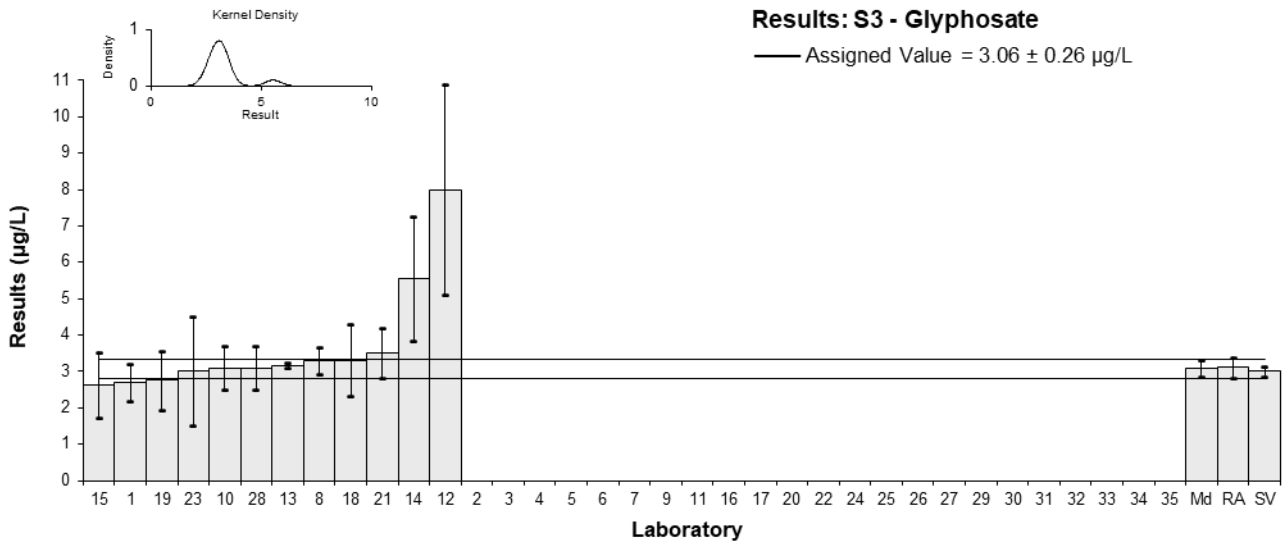


Figure 15

## 6 DISCUSSION OF RESULTS

### 6.1 Assigned Value

The assigned values for all scored analytes were the robust averages of participants' results. If there were results less than 50% and greater than 150% of the robust average, these were excluded from the calculation of each assigned value.<sup>3,4</sup> The robust averages and associated expanded uncertainties were calculated using the procedure described in ISO 13528.<sup>6</sup> The calculation of the expanded uncertainty for robust averages is presented in Appendix 3, using Sample S1 fenthion as an example.

A comparison of the assigned values and spiked values is presented below in Table 20. For the scored analytes, assigned values were within the range of 54% to 104% of the spiked values. Similar ratios have been observed in previous NMIA Pesticides in River Water PT studies, and an assigned value was set if there was a reasonable consensus of results.

Table 20 Comparison of Assigned Value and Spiked Value

Sample	Analyte	Assigned Value (µg/L)	Spiked Value (µg/L)	Assigned Value / Spiked Value (%)
S1	Aldrin	2.05*	18.2	11
	Diuron	3.29	3.68	89
	Fenitrothion	1.11	1.30	85
	Fenthion	25.3	30.0	84
	Imazapyr	21.6	21.0	103
	Metolachlor	0.476	0.490	97
S2	Atrazine	2.16	2.49	87
	Deltamethrin	3.54*	19.1	18
	Diazinon	0.207	0.251	82
	Dimethoate	9.2	16.9	54
	Fenthion	2.70	3.02	89
	Metsulfuron-methyl	3.51	3.52	100
S3	AMPA	7.4	7.10	104
	Glyphosate	3.06	3.00	102

\*Robust Average (assigned value not set).

No assigned values were set for Sample S1 aldrin and Sample S2 deltamethrin as participants' results were too varied, and the consensus was significantly lower than the spiked value. Participants may still compare their results with the descriptive statistics and spiked value as presented in Section 5.

**Traceability:** The consensus of participants' results is not traceable to any external reference, so although expressed in SI units, metrological traceability has not been established.

### 6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an evaluation of the expanded uncertainty associated with their results and the basis of this uncertainty evaluation. It is a requirement of ISO/IEC 17025 that laboratories have procedures to evaluate the uncertainty of chemical measurements and to report this uncertainty in specific circumstances, including when the client's instruction so requires.<sup>8</sup>

Of 268 numeric results submitted for the analytes of interest in this study, 249 (93%) were reported with an expanded MU. Participants used a wide variety of procedures to evaluate their uncertainty (Tables 3 and 4). The magnitude of reported uncertainties was within the range of 2.0% to 88% relative to the result. In general, an expanded uncertainty of less than 15% relative may be unrealistically small for the routine measurement of a pesticide residue, while an uncertainty of greater than 50% relative may be too large to be fit-for-purpose. Of the 249 MUs reported for this study, 36 were less than 15% relative, and 11 were greater than 50% relative. Uncertainties associated with results returning an acceptable *z*-score but an unacceptable *E<sub>n</sub>*-score may have been undervalued.

Laboratories 4, 15, 32, and 33 did not report an uncertainty for at least one of their numeric results. These participants all reported being accredited to ISO/IEC 17025.

Participants were requested to report the coverage factor associated with their uncertainty (Table 3). Twenty-one participants reported a coverage factor of 2, and one participant reported a coverage factor of 2.26.

Laboratories 2, 15, and 16 attached evaluations of the expanded MU for results reported as less than their limit of reporting (LOR). An evaluation of uncertainty expressed as a value cannot be attached to a result expressed as a range.<sup>9</sup>

In some cases, the results were reported with an inappropriate number of significant figures. Including too many significant figures may inaccurately reflect the precision of measurements. The recommended format is to write uncertainty to no more than two significant figures, and then to write the result with the corresponding number of decimal places. For example, instead of  $1.954 \pm 0.586$  mg/kg, report  $1.95 \pm 0.59$  mg/kg.<sup>9</sup>

### 6.3 z-Score

The *z*-score compares the participant's deviation from the assigned value based on the standard deviation for proficiency assessment (SDPA). The SDPA defines acceptable performance in a PT study. SDPAs equivalent to 15% PCV were used to calculate *z*-scores. CVs predicted by the Thompson-Horwitz equation,<sup>7</sup> between-laboratory CVs and SDPAs (as PCV) for this study are presented for comparison in Table 21.

Table 21 Comparison of Thompson-Horwitz CV, Between-Laboratory CV and SDPA\*

Sample	Analyte	Assigned Value (µg/L)	Thompson-Horwitz CV (%)	Between-Laboratory CV (%)	SDPA (as PCV, %)
S1	Aldrin	2.05**	22	66	Not Set
S1	Diuron	3.29	22	22	15
S1	Fenitrothion	1.11	22	18	15
S1	Fenthion	25.3	22	22	15
S1	Imazapyr	21.6	22	28	15
S1	Metolachlor	0.476	22	15	15
S2	Atrazine	2.16	22	15	15
S2	Deltamethrin	3.5**	22	55	Not Set
S2	Diazinon	0.207	22	21	15
S2	Dimethoate	9.2	22	22	15
S2	Fenthion	2.70	22	15	15

Sample	Analyte	Assigned Value (µg/L)	Thompson-Horwitz CV (%)	Between-Laboratory CV (%)	SDPA (as PCV, %)
S2	Metsulfuron-methyl	3.51	22	19	15
S3	AMPA	7.4	22	19	15
S3	Glyphosate	3.06	22	11	15

\*Thompson-Horwitz CV calculated from the assigned value. The between-laboratory CV is the between-laboratory CV with outliers removed, if applicable. Shaded cells represent between-laboratory CVs higher than both the SDPA and the Thompson-Horwitz CV for scored analytes.

\*\*Robust Average (assigned value not set).

To account for possible low bias in the consensus value due to laboratories using inefficient analytical or extraction techniques, six *z*-scores were adjusted for Sample S2 dimethoate. A maximum acceptable result was set as the spiked value plus two SDPAs of the spiked value. Results lower than the maximum acceptable result but with a *z*-score greater than 2.0 had their *z*-score adjusted to 2.0. This ensured that any participants reporting results close to the spiked value were not penalised. *z*-Scores for results greater than the maximum acceptable result, and *z*-scores less than 2.0, were left unaltered.

Of 222 results for which *z*-scores were calculated, 178 (80%) returned a score of  $|z| \leq 2.0$ , indicating an acceptable performance.

Laboratory 23 reported numeric results for all scored analytes in this study.

Eighteen participants received acceptable *z*-scores for all reported results that were scored: 10 (10), 28 (10), 18 (9), 19 (8), 20 (8), 5 (7), 17 (7), 1 (6), 21 (6), 22 (6), 9 (5), 30 (5), 6 (2), 25 (4), 26 (4), 11 (3), 34 (3), and 8 (2).

Laboratory 24 did not report a numeric result for any of the analytes of interest in this study.

The dispersal of *z*-scores is presented by laboratory in Figure 16, and by analyte in Figure 17.

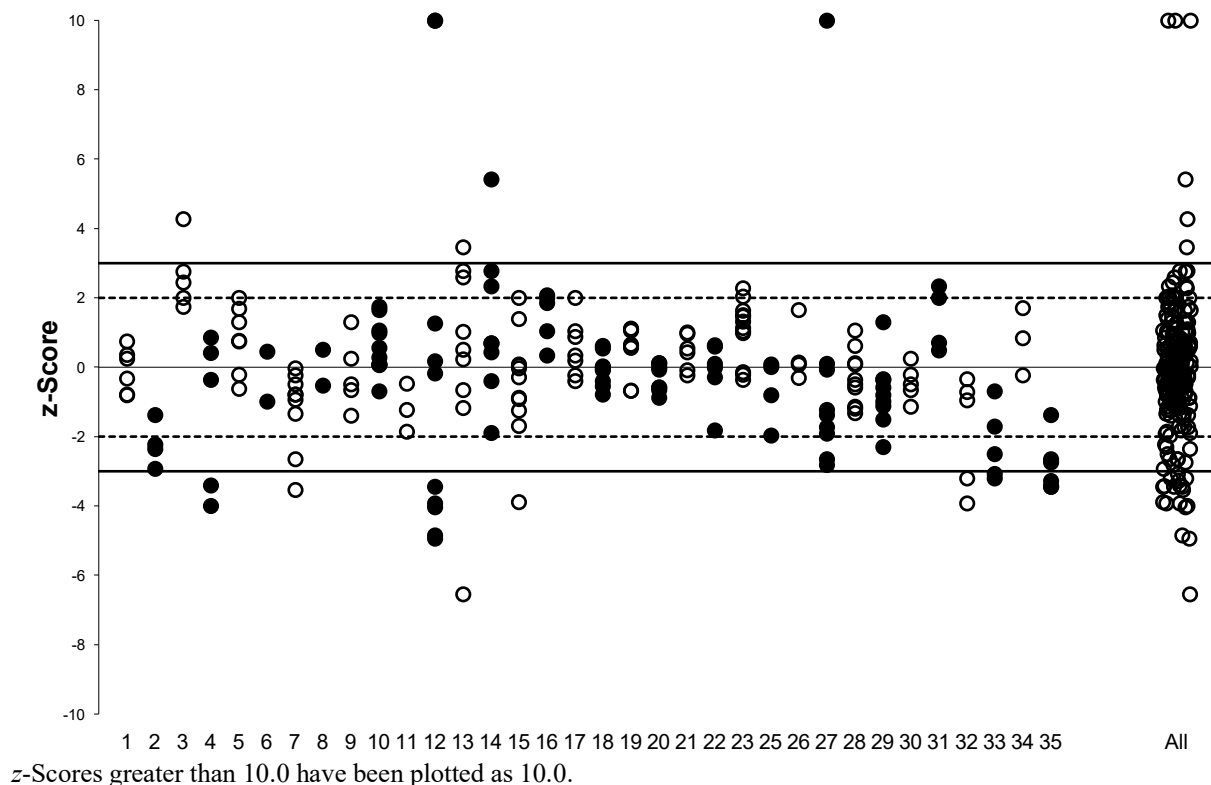
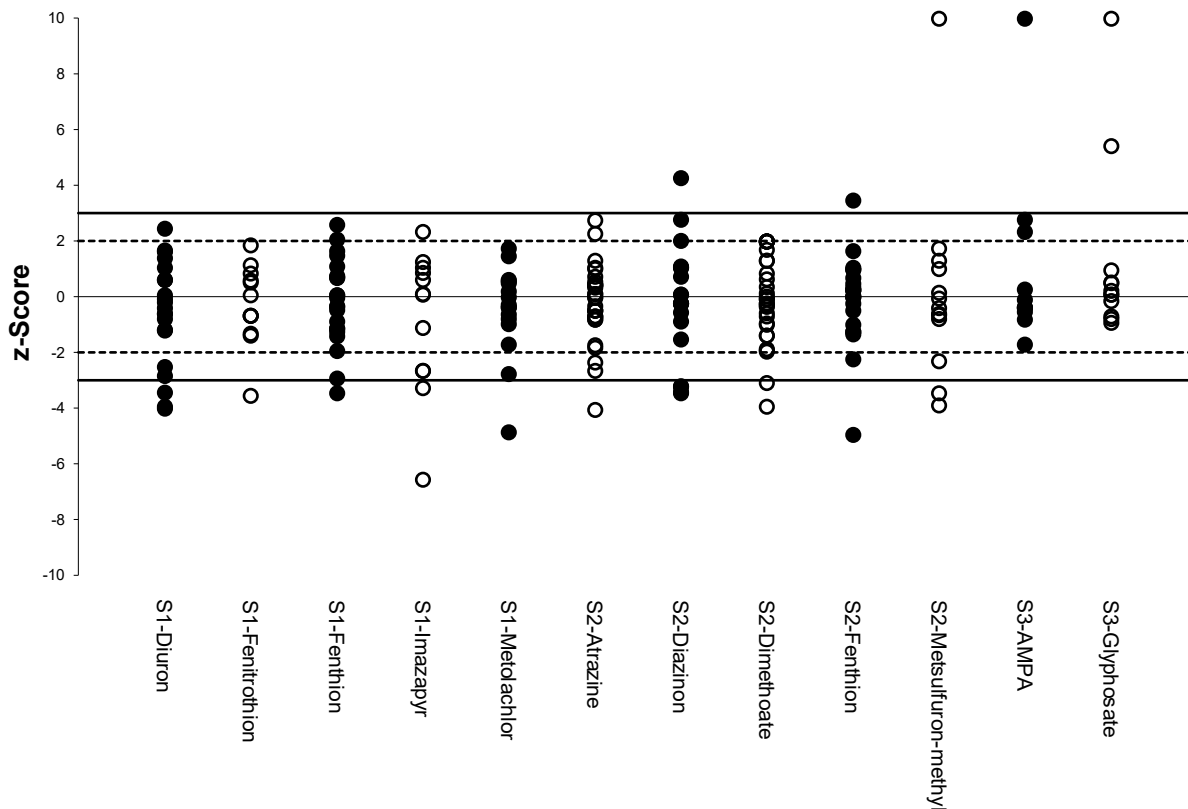


Figure 16 *z*-Score Dispersal by Laboratory



z-Scores greater than 10.0 have been plotted as 10.0.

Figure 17 z-Score Dispersal by Analyte

#### 6.4 $E_n$ -Score

$E_n$ -scores can be interpreted in conjunction with z-scores, as an unacceptable  $E_n$ -score can either be caused by issues with measurement, uncertainty evaluation, or both. If a participant did not report an expanded MU with a result, an expanded uncertainty of zero (0) was used to calculate the  $E_n$ -score. For results whose z-scores were adjusted as discussed in Section 6.3, no  $E_n$ -score has been calculated.

Of 216 results for which  $E_n$ -scores were calculated, 165 (76%) returned a score of  $|E_n| < 1.0$ , indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratory 23 returned acceptable  $E_n$ -scores for all 12 scored analytes.

Eighteen participants received acceptable  $E_n$ -scores for all reported results that were scored: 10 (10), 28 (10), 18 (9), 19 (8), 20 (8), 1 (6), 5 (6), 17 (6), 21 (6), 22 (6), 9 (5), 30 (5), 16 (4), 26 (4), 31 (3), 34 (3), 6 (2), and 8 (2).

All results reported by Laboratories 33 and 35 returned unacceptable  $E_n$ -scores. Laboratory 33 did not report any uncertainties; for those results reported by this participant returning acceptable z-scores, if reasonable and fit-for-purpose uncertainties had been reported, those results may have returned acceptable  $E_n$ -scores.

The dispersal of  $E_n$ -scores by laboratory is presented in Figure 18.

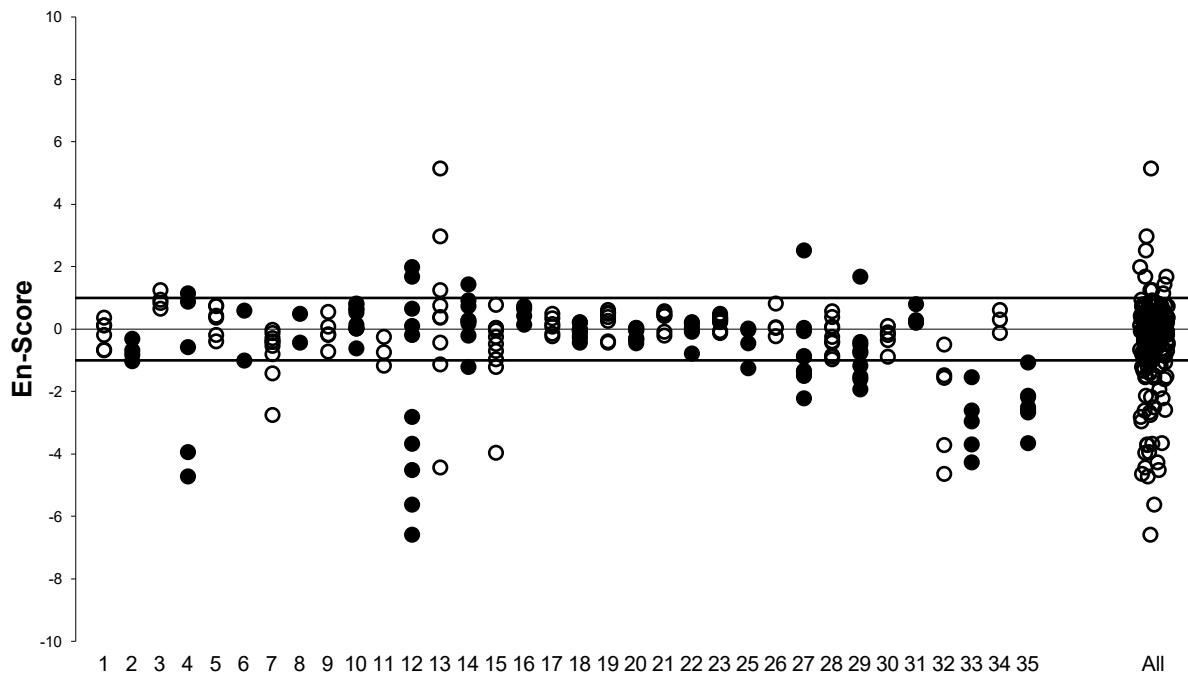


Figure 18  $E_n$ -Score Dispersal by Laboratory

### 6.5 False Negatives

Table 22 presents false negative results. These are analytes present in the samples which a participant tested for but did not report a numeric result; for example, participants reporting a ‘less than’ result ( $< x$ ) when the assigned value was higher than their limit of reporting (LOR), or participants that did not report anything. For analytes where no assigned value was set, results have only been considered to be false negatives where the consensus value and spiked value (if applicable) were significantly higher than the participants’ LOR (i.e. the consensus value minus the expanded uncertainty, and the spiked value minus the expanded uncertainty, were both greater than the LOR), or if no value was reported.

Table 22 False Negatives

Lab. Code	Sample	Analyte	Assigned Value ( $\mu\text{g/L}$ )	Spiked Value ( $\mu\text{g/L}$ )	Result* ( $\mu\text{g/L}$ )
6	S1	Diuron	3.29	3.68	<1
6	S1	Fenitrothion	1.11	1.30	<1
7	S1	Metolachlor	0.476	0.490	<0.01
9	S2	Diazinon	0.207	0.251	<0.2
10	S1	Metolachlor	0.476	0.490	<0.01
12	S1	Fenitrothion	1.11	1.30	<0.01
12	S2	Diazinon	0.207	0.251	<0.01
14	S1	Fenitrothion	1.11	1.30	< 0.01
14	S1	Metolachlor	0.476	0.490	< 0.2
14	S2	Deltamethrin	3.5**	19.1	< 0.05
14	S2	Diazinon	0.207	0.251	< 0.1
14	S2	Metsulfuron-methyl	3.51	3.52	< 2.5
20	S2	Diazinon	0.207	0.251	<0.2

Lab. Code	Sample	Analyte	Assigned Value (µg/L)	Spiked Value (µg/L)	Result* (µg/L)
26	S1	Fenitrothion	1.11	1.30	<0.5
27	S1	Metolachlor	0.476	0.490	<0.01
29	S1	Fenitrothion	1.11	1.30	<1
30	S2	Diazinon	0.207	0.251	<0.2
31	S1	Diuron	3.29	3.68	NR
31	S1	Imazapyr	21.6	21.0	NR
31	S1	Metolachlor	0.476	0.490	NR
31	S2	Atrazine	2.16	2.49	NR
31	S2	Deltamethrin	3.5**	19.1	NR
31	S2	Metsulfuron-methyl	3.51	3.52	NR

\*Results reported as NR may or may not be false negatives, depending on the participants' actual LOR.

\*\*Robust Average (assigned value not set).

## 6.6 Reporting of Additional Analytes

Table 23 presents analytes reported by participants that were not spiked into the test samples by the study coordinator.

Table 23 Analytes Reported by Participants Not Spiked in the Test Samples

Lab. Code	Sample	Analyte	Result (µg/L)	Uncertainty (µg/L)	Recovery (%)
3	S1	Picloram	0.315	0.0945	NR
3	S1	Haloxypop	0.285	0.0855	NR
3	S2	Haloxypop	0.086	0.0258	NR
4	S2	Aldrin	0.264	NT	109
7	S1	Picloram	0.25	0.075	65
7	S2	2,4-D	0.1	0.03	NR
10	S1	Picloram	0.32	0.05	NR
10	S2	Picloram	0.16	0.03	NR
13	S1	Hexazinone	0.00171	0.0004	66
13	S1	Propiconazole	0.00502	0.00148	53
13	S1	Simazine	0.000954	0.000387	56
13	S2	Hexazinone	0.00157	0.00022	69
13	S2	Metolachlor	0.00112	0.000163	55
13	S2	Propiconazole	0.00593	0.000642	55
13	S2	Simazine	0.00674	0.00175	55
17	S1	Picloram	0.30	0.08	92
17	S2	Picloram	0.16	0.04	92
21	S1	Picloram	0.205	0.039	NR
23	S1	Picloram	0.3	0.15	120
27	S1	Picloram	0.25	0.0625	65
32	S2	Aldrin	0.2244	NT	111

Lab. Code	Sample	Analyte	Result (µg/L)	Uncertainty (µg/L)	Recovery (%)
33	S2	Aldrin	0.2453	NT	109
34	S2	Aldrin	0.19	0.06	73

### 6.7 Range of Pesticides Analysed by Participants

Participants were provided with a list of potential pesticides that could have been spiked into Samples S1 and S2 (Table 2), in addition to AMPA and glyphosate in Sample S3. In total, 13 different pesticides were used for spiking in this study, with one pesticide being spiked into both Samples S1 and S2. Participants were not required to test for all potential pesticides, and were requested to report ‘NT’ (for ‘Not Tested’) for any that they did not analyse the samples for.

Laboratories **12, 14, 20, 23,** and **31** reported that they tested for all spiked analytes. All participants, except for Laboratory **24**, reported at least one spiked analyte, with the proportion of analytes being reported by each participant ranging from 15% to 100%.

Of the spiked analytes in this study, diazinon was tested for by the highest proportion of participants (97%), while imazapyr was tested for by the lowest proportion of participants (35%).

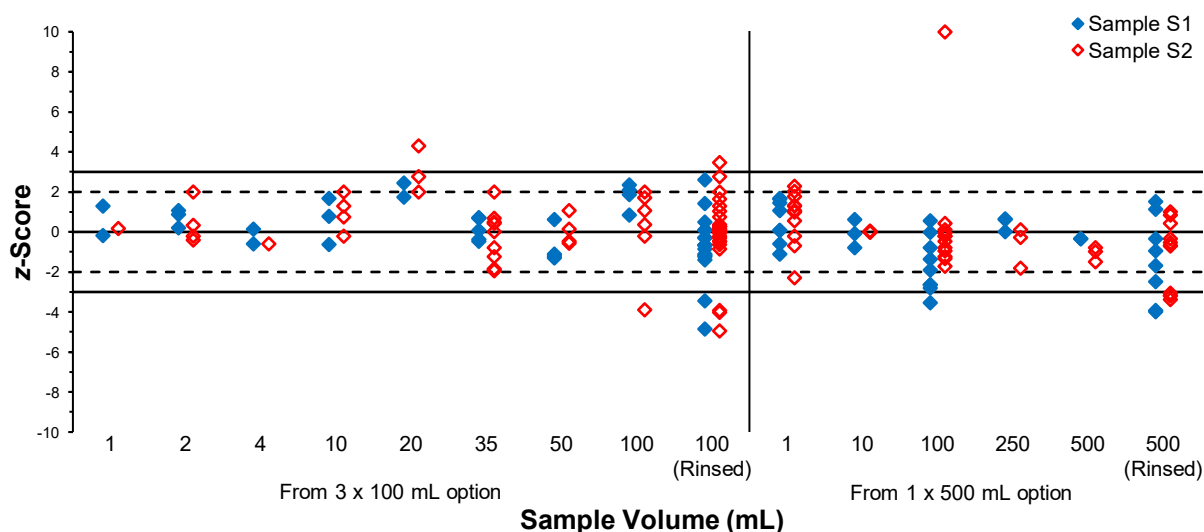
### 6.8 Participants’ Analytical Methods

Results that were removed from all statistical calculations in Section 5 have also been removed from all discussion in this section. Where charts refer to  $n = x$ , this corresponds to  $x$  number of participants using that methodology.

Participants used a variety of analytical methods for the test samples (Appendix 4).

#### Samples S1 and S2

For Samples S1 and S2, participants were given the option of samples as 1 x 500 mL (12 participants) or as 3 x 100 mL (22 participants), depending on what suited their laboratory’s method. Participants reported test portions ranging from 1 mL to 500 mL. A comparison of z-scores and sample volume used for scored analytes is presented in Figure 19. There was no significant trend or correlation observed in this study, regardless of whether the participant used only part of the bottle provided, or, if they used the whole bottle, whether they rinsed the bottle or not.



z-Scores greater than 10.0 have been plotted at 10.0.

Figure 19 Samples S1 and S2 z-Score vs Sample Volume

For the analytes in Samples S1 and S2, participants reported using direct injection (DI), or different extractions techniques such as liquid-liquid extraction (LLE), solid-phase extraction (SPE) and ‘Quick, Easy, Cheap, Effective, Rugged and Safe’ extraction (QuEChERS). For extraction solvents, participants reported using acetone (Ace), acetonitrile (ACN), dichloromethane (DCM), ethyl acetate (EtOAc), water (H<sub>2</sub>O), hexane (Hex), methanol (MeOH), pentane (Pent) or mixtures of these solvents. Most participants reported that they performed multiple steps for their extraction. Extraction time varied significantly between participants, going up to 90 minutes for some participants. There was also variation in the extract concentration temperature used (some participants opted for ambient temperatures, and others heated the extract), and how long extracts were concentrated for (up to 90 minutes for some participants). Some participants reported a further clean-up step, such as centrifugation (Centr.) or filtration (Filtr.) for certain analytes. Participants reported using gas chromatography (GC) coupled to electron capture detection (ECD), mass spectrometry (MS) or tandem mass spectrometry (MS/MS), and liquid chromatography (LC) coupled to MS/MS or diode array detection (DAD).

Plots of numeric results and methodology employed (extraction technique, extraction solvent, clean-up and measurement instrument) for scored analytes in this study are presented in Figures 20 to 29. Participants results yielding unacceptable z scores ( $|z| \geq 3.0$ ) have been circled for reference.

In Sample S1 diuron, results returned by participants using SPE were generally biased low regardless of other parameters in their methodology.

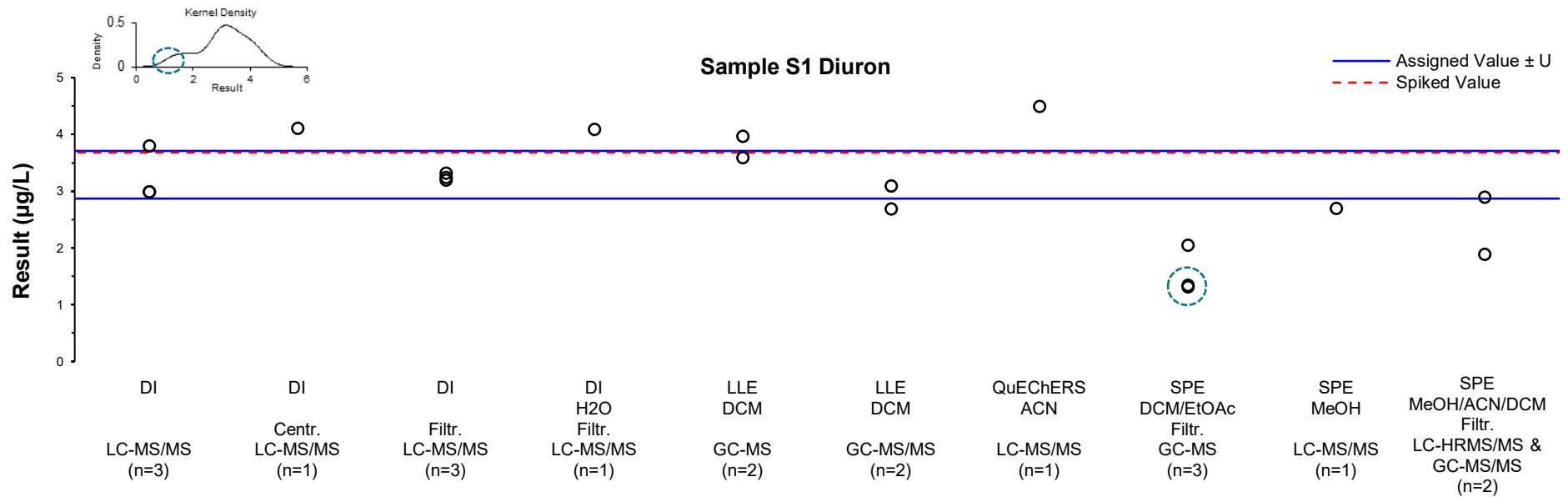


Figure 20 Sample S1 Diuron Result vs Methodology

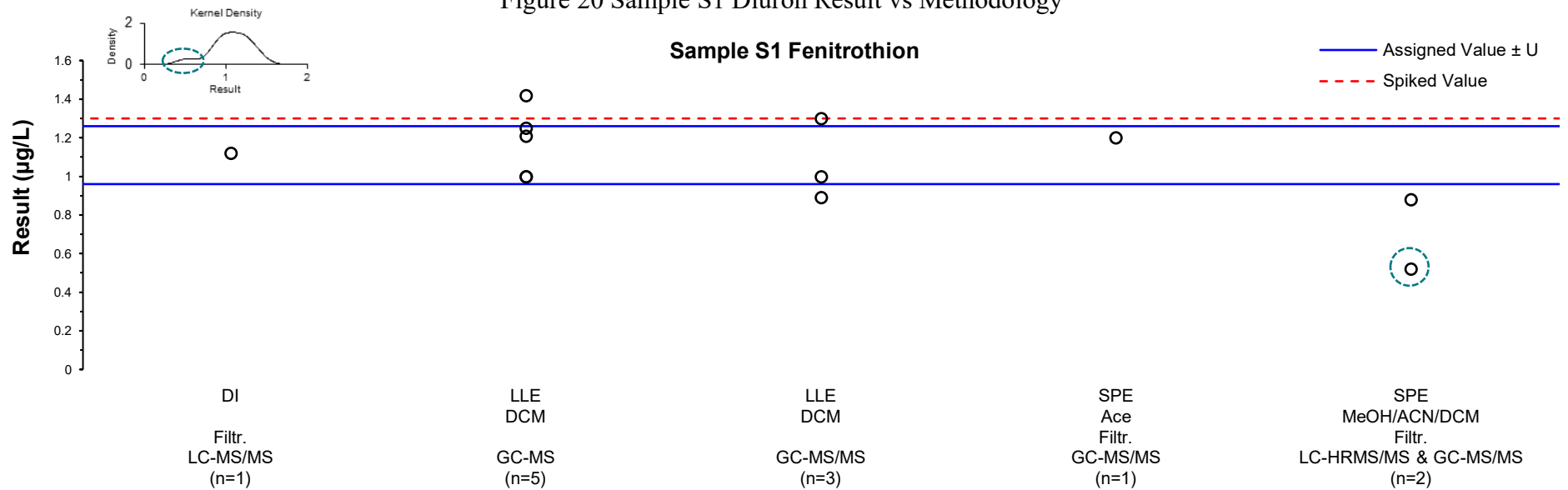


Figure 21 Sample S1 Fenitrothion Result vs Methodology

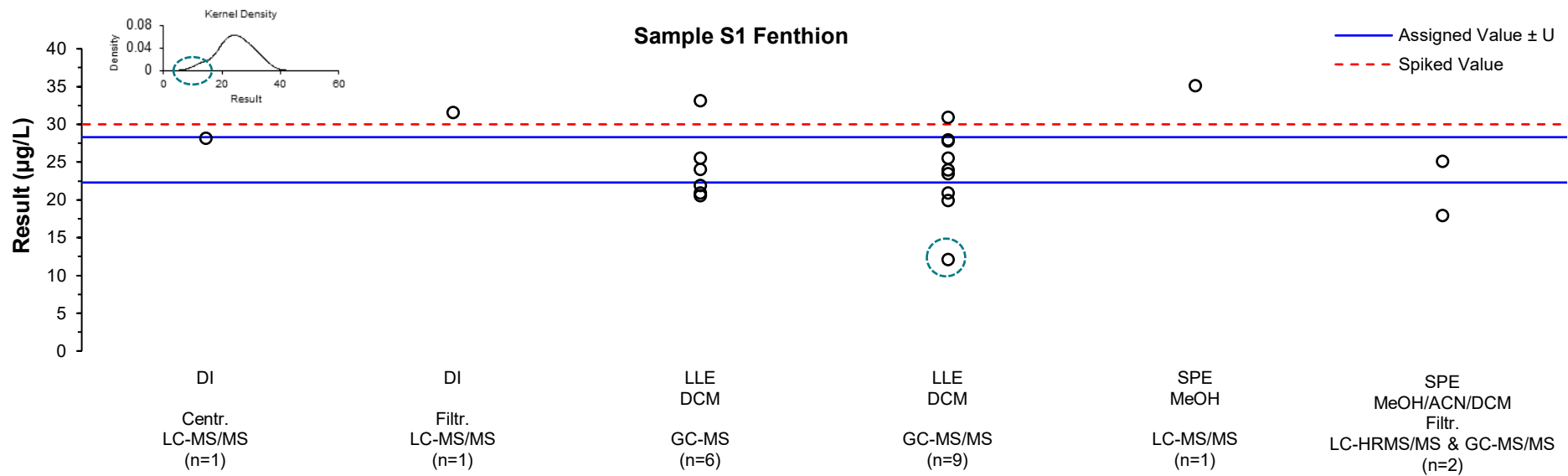


Figure 22 Sample S1 Fenthion Result vs Methodology

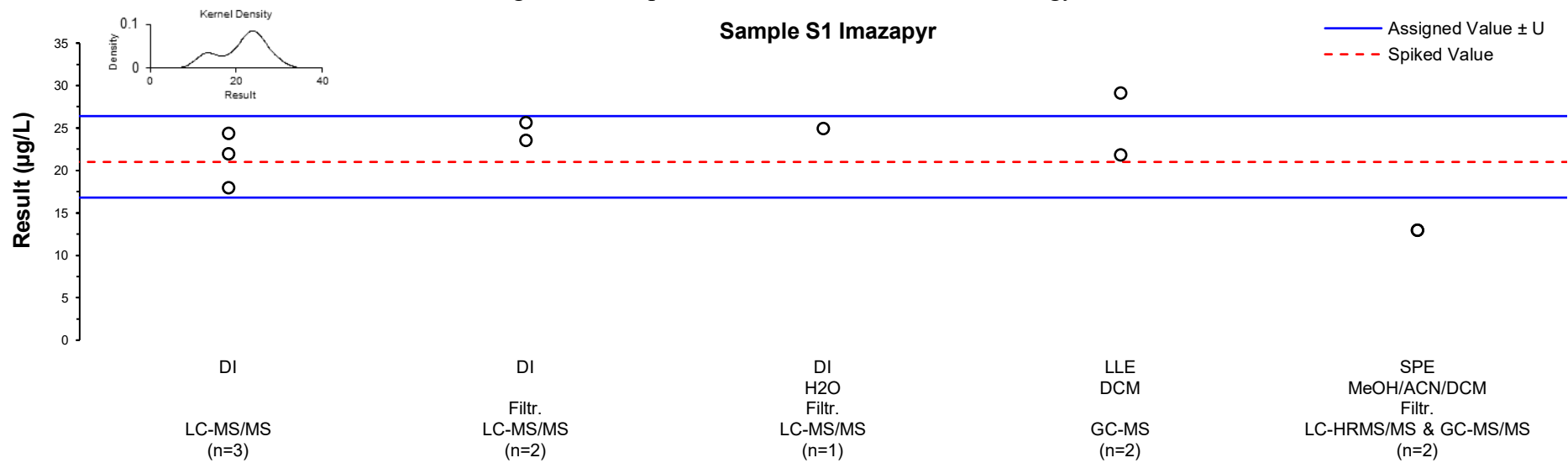


Figure 23 Sample S1 Imazapyr Result vs Methodology

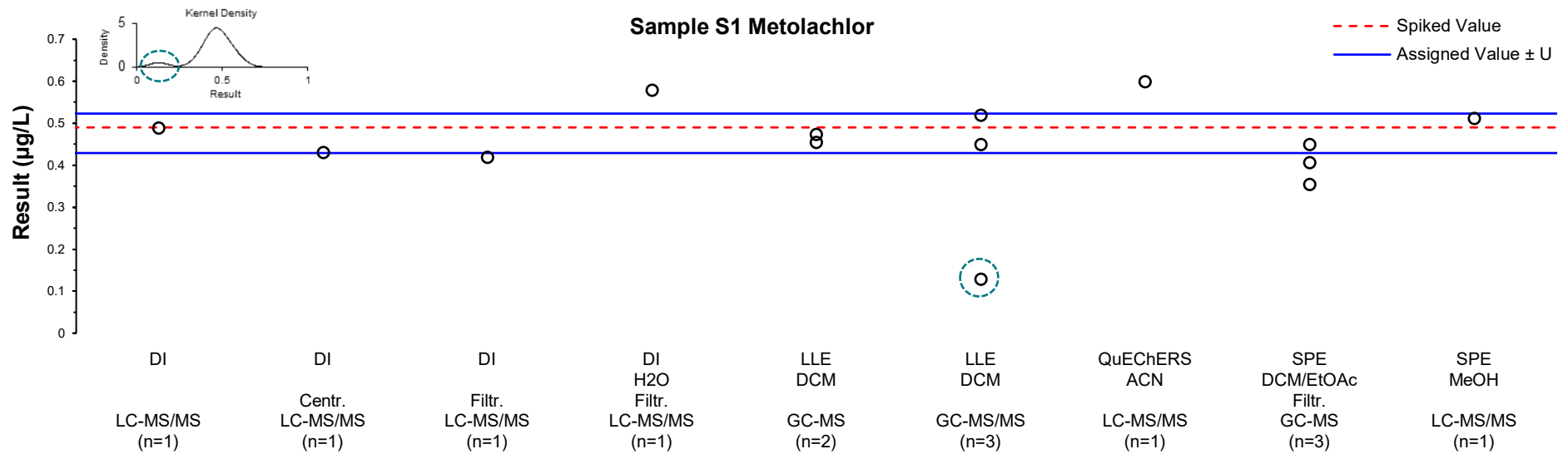


Figure 24 Sample S1 Metolachlor Result vs Methodology

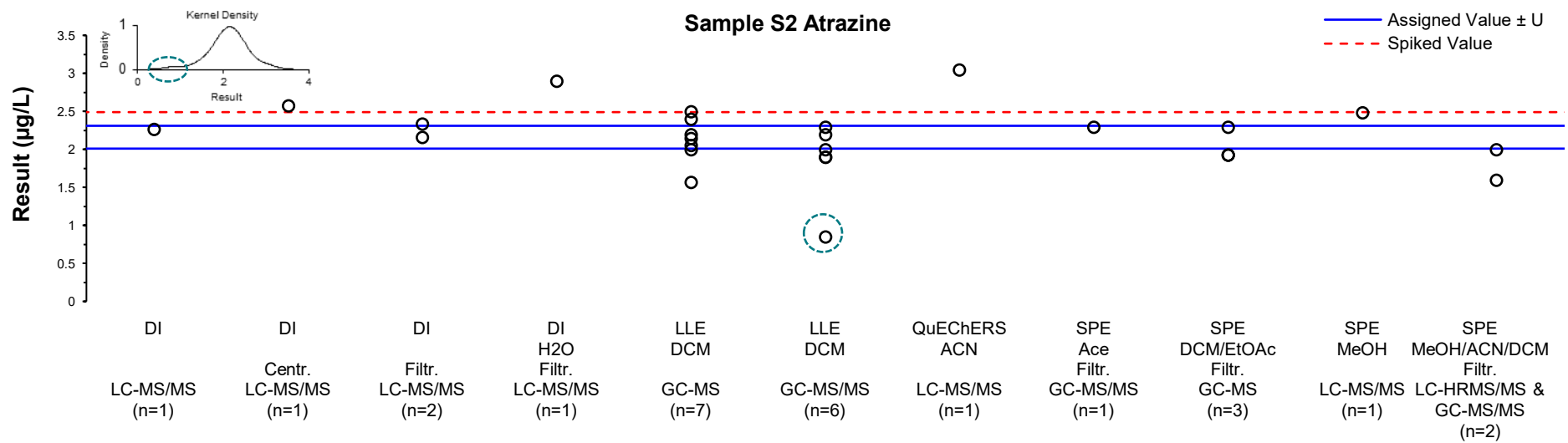


Figure 25 Sample S2 Atrazine Result vs Methodology

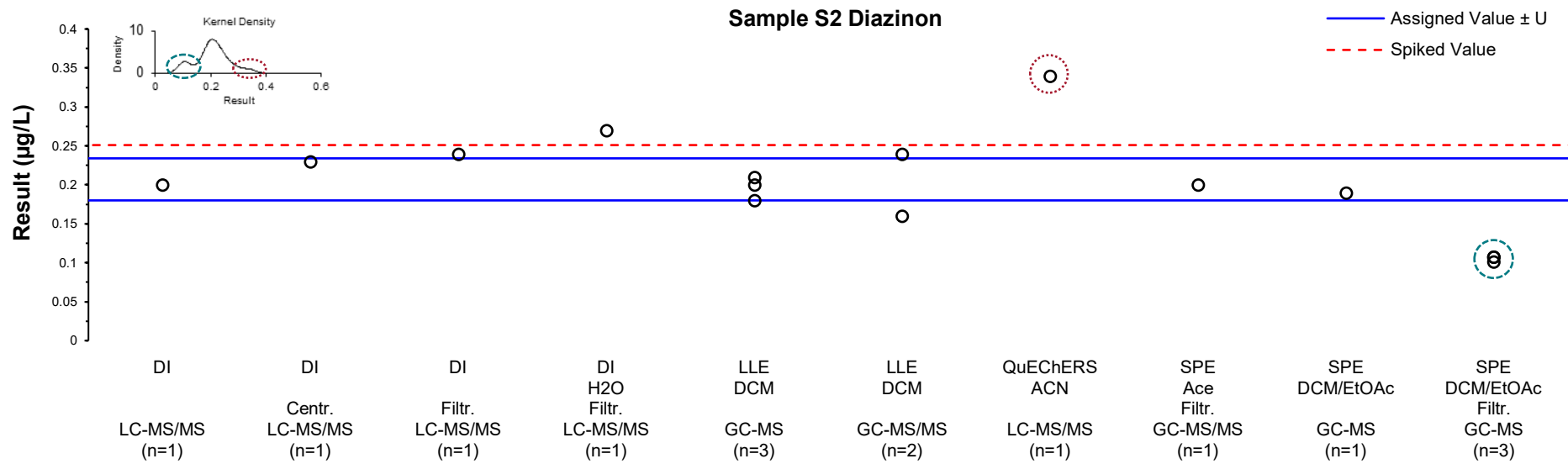


Figure 26 Sample S2 Diazinon Result vs Methodology

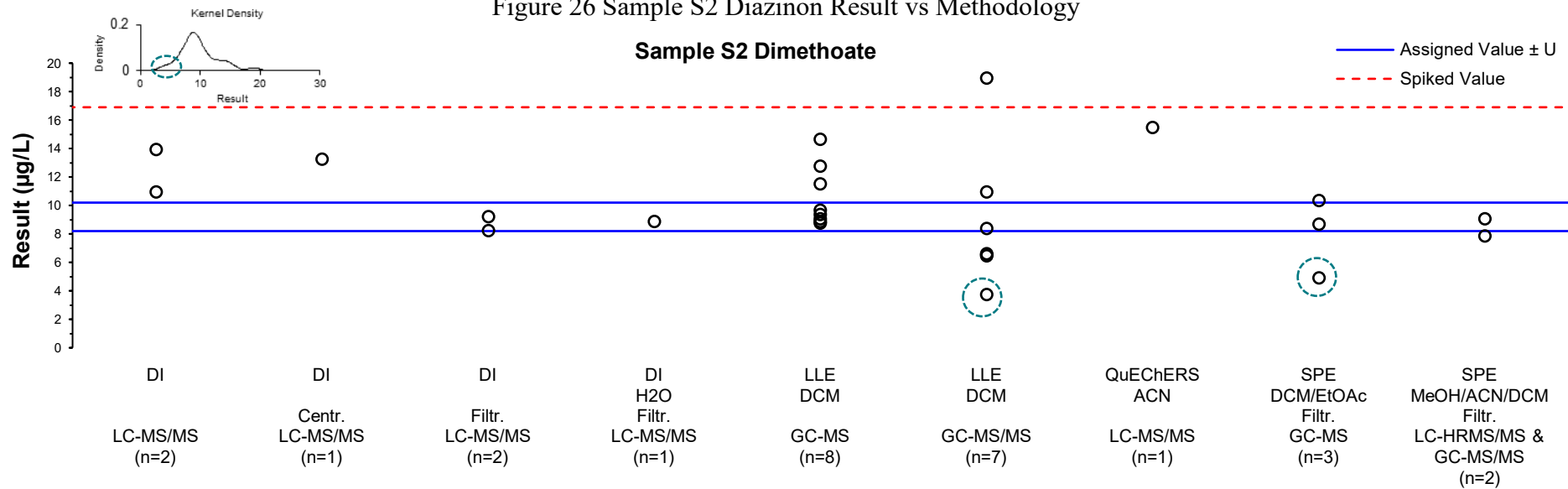


Figure 27 Sample S2 Dimethoate Result vs Methodology

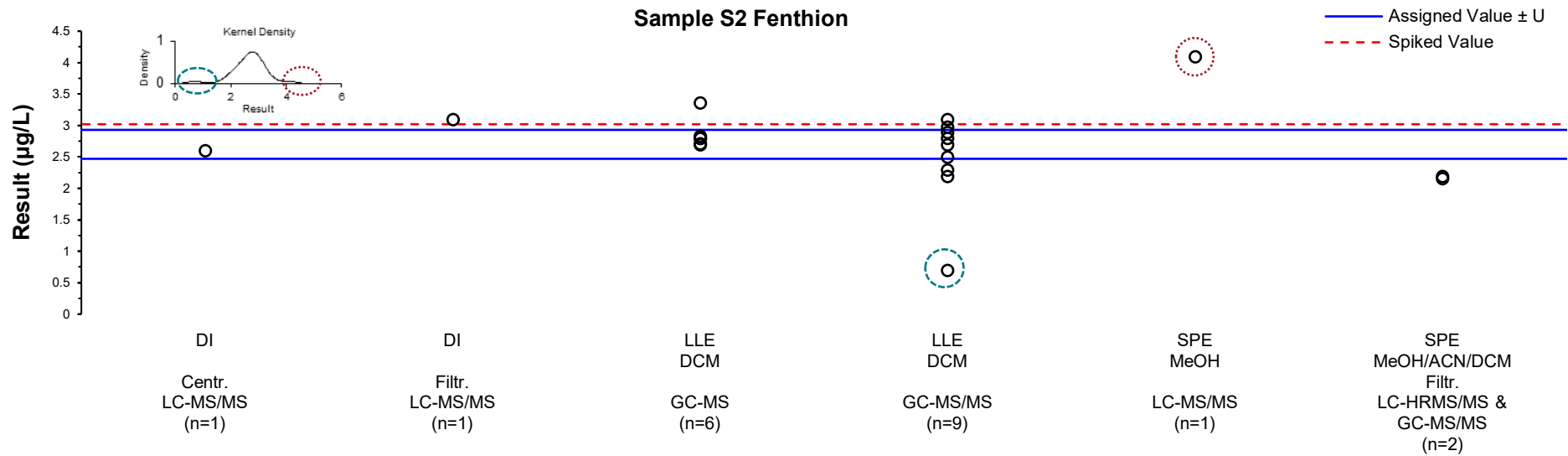


Figure 28 Sample S2 Fenthion Results vs Methodology

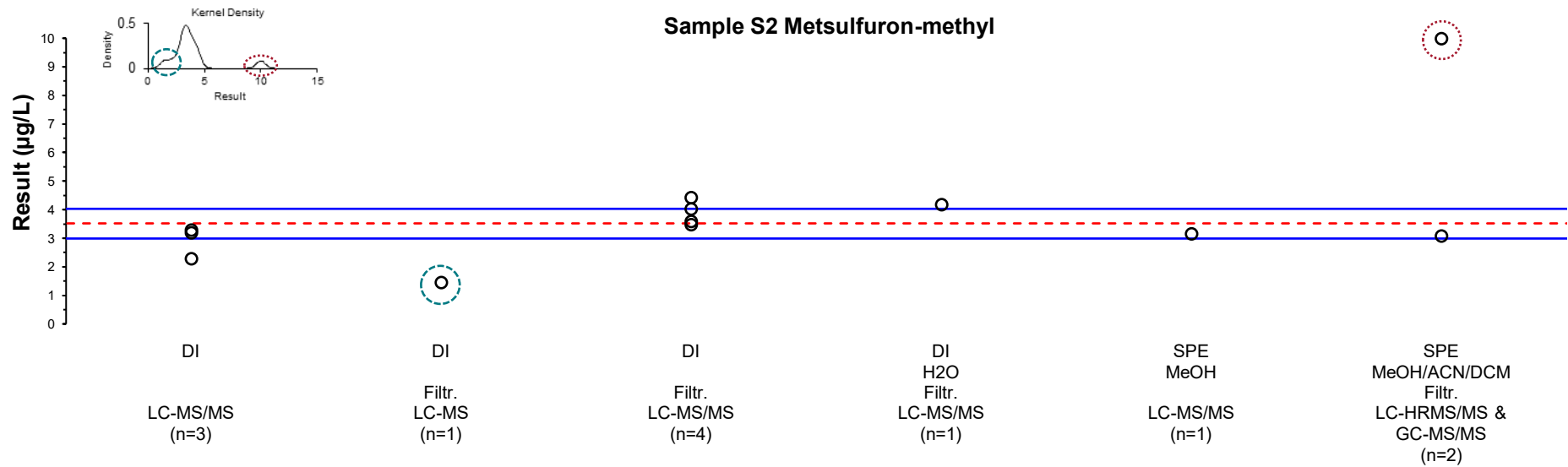


Figure 29 Sample S2 Metsulfuron-methyl Results vs Methodology

### Sample S3

For Sample S3, participants were supplied a 500 mL bottle. Participants reported test portions ranging from 0.1 mL to 10 mL. A comparison of z-scores and sample volume used for scored analytes is presented in Figure 30; there was no evident correlation in this study.

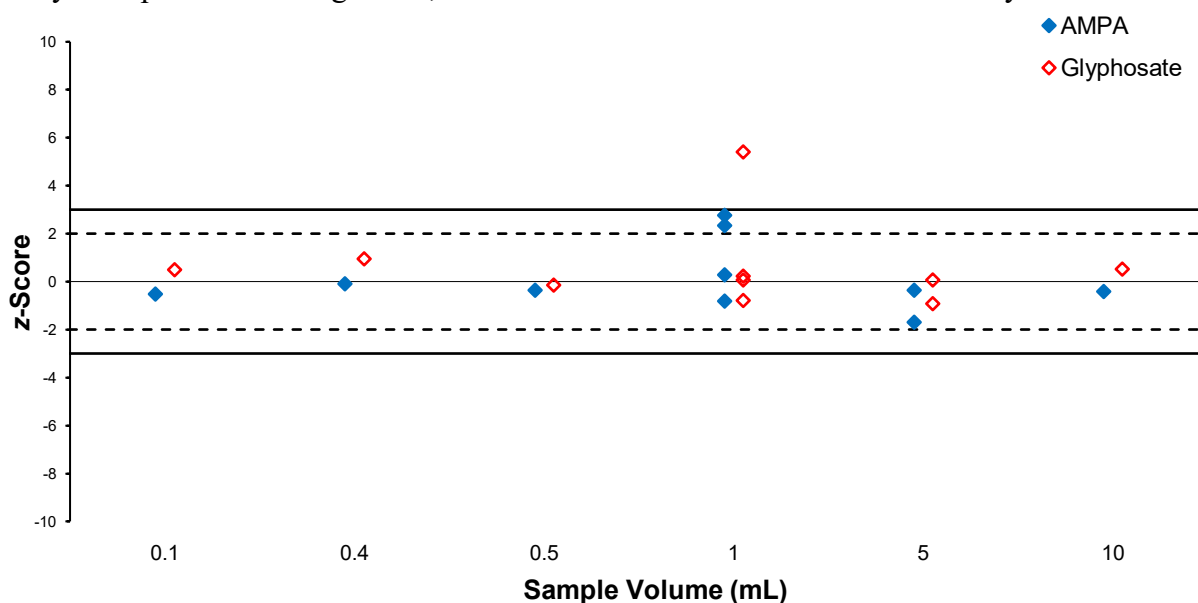


Figure 30 Sample S3 z-Score vs Sample Volume

For Sample S3, participants reported extracting using DI or LLE. Most participants reported derivatisation pre-column using fluorenylmethyloxycarbonyl group (FMOC) or a mixture of MeOH and acetic anhydride (Ac<sub>2</sub>O). Participants used LC techniques (including being reported as high performance LC (HPLC)), coupled with MS/MS or fluorescence detection (FLD).

Plots of numeric results and methodology employed (extraction technique, derivatisation and measurement instrument) for Sample S3 analytes are presented in Figures 31 and 32. Participants results yielding unacceptable z scores ( $|z| \geq 3.0$ ) have been circled for reference.

In this study, participants used a variety of methodologies and no significant trends were observed.

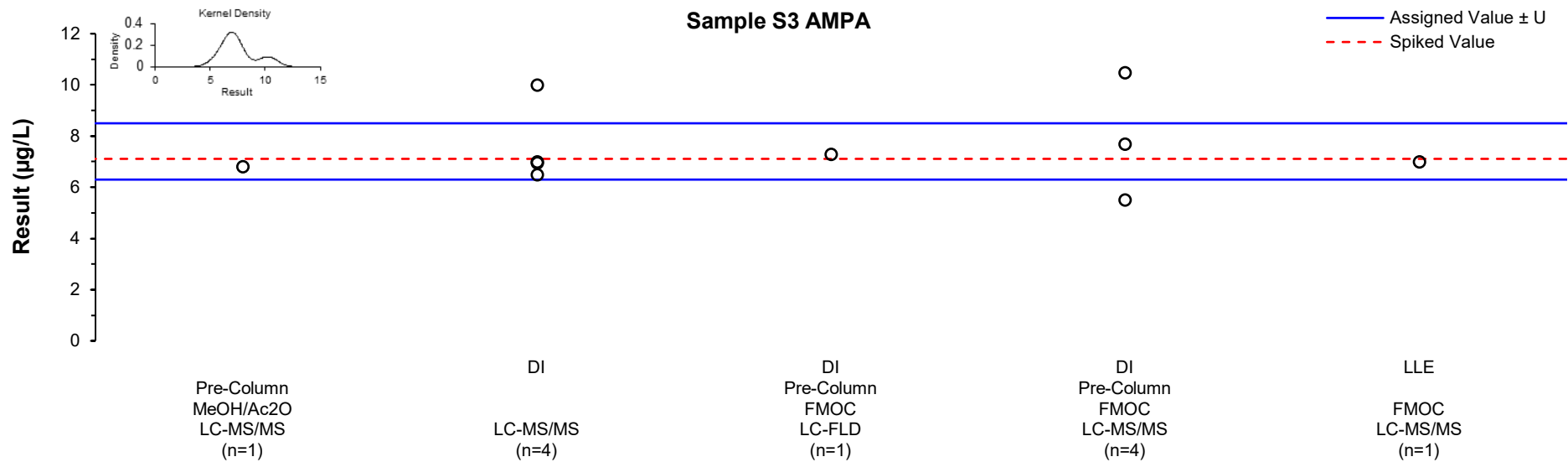


Figure 31 Sample S3 AMPA Result vs Methodology

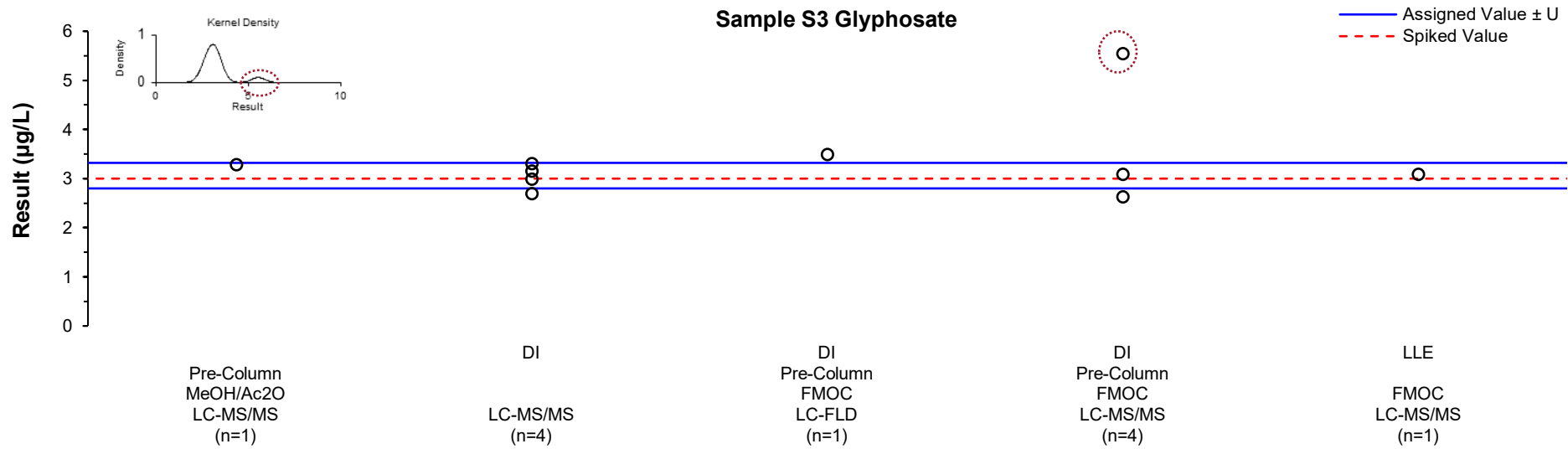


Figure 32 Sample S3 Glyphosate Result vs Methodology

Participants were requested to analyse the samples using their routine test method and to report a single result as they would to a client, that is, reported for recovery or not, according to their standard procedure. Results reported in this way reflect the true variability of results reported by laboratories to clients. Laboratories **1, 4, 6, 7, 8, 12, 13, 14, 16, 17, 18, 23, 27, 29, 30, 31, 32, 33, 34,** and **35** reported recoveries for at least one analyte considered in this study, with reported recoveries ranging from 21% to 133%. Laboratories **7, 8, 13, 21, 27,** and **35** reported that they corrected their results for recoveries.

## 6.9 Certified Reference Materials

Participants were requested to indicate whether certified standards or matrix reference materials had been used as part of the quality assurance for their analysis.

Twenty-two participants reported using certified standards, and one participant reported using both certified standards and matrix reference materials. The following were listed:

- Accustandard
- Merck
- o2Si
- PM Separations
- ISO 17034 standards

These materials may or may not meet the internationally recognised definition of a certified reference material:

*‘reference material, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures’<sup>10</sup>*

## 6.10 Summary of Participants’ Results and Performances

Summaries of participants’ results and performances in this PT study for scored analytes are presented in Tables 24 to 26 and Figure 33.

Table 24 Summary of Participants’ Results in Sample S1\*

Lab. Code	Diuron	Fenitrothion	Fenthion	Imazapyr	Metolachlor
AV	3.29	1.11	25.3	21.6	0.476
SV	3.68	1.30	30.0	21.0	0.490
1	NT	NT	24.1	NT	NT
2	NT	NT	14.2	NT	NT
3	4.5	NT	NT	NT	0.6
4	1.3204	NT	NT	NT	0.4502
5	4.12	<2	28.2	NT	0.432
6	<1	<1	NT	NT	<1
7	2.9	0.52	25.2	13	<0.01
8	NS	NS	NS	NS	NS
9	NT	1	20	NT	<2
10	3.33	1.12	31.6	NT	<0.01
11	NT	< 2	23.5	NT	NT

Lab. Code	Diuron	Fenitrothion	Fenthion	Imazapyr	Metolachlor
12	3.2	<0.01	12.19	25.7	0.13
13	2.71	NT	35.17	0.371	0.512
14	3.1	< 0.01	27.9	29.19	< 0.2
15	3.98	<2	20.6	21.9	0.456
16	NT	1.42	33.2	NT	NT
17	3.81	NT	NT	24.43	0.49
18	3.25	NT	NT	23.6	0.42
19	3.595	<2.5	29.5	NT	0.517
20	3	1	22	22	<2
21	NT	1.2	NT	NT	NT
22	3.6	1.21	NT	NT	0.475
23	4.1	1.3	31	25	0.58
24	NT	NT	NT	NT	NT
25	< 5	< 2	25.6	NT	< 1
26	NT	<0.5	25.6	NT	NT
27	1.9	0.88	18	13	<0.01
28	2.7	0.89	21	NT	0.52
29	3.0	<1	24	18	0.45
30	NT	1	21	NT	<2
31	NR	<2	28	NR	NR
32	1.3503	NT	NT	NT	0.4075
33	2.0571	NT	NT	NT	0.3549
34	NT	1.25	NT	NT	NT
35	1.6	NT	NT	11	0.28

\*All values are in µg/L. Shaded cells are results which returned a questionable or unacceptable z-score for scored analytes. AV = Assigned Value, SV = Spiked Value.

Table 25 Summary of Participants' Results in Sample S2 \*

Lab. Code	Atrazine	Diazinon	Dimethoate	Fenthion	Metsulfuron-methyl
AV	2.16	0.207	9.2	2.70	3.51
SV	2.49	0.251	16.9	3.02	3.52
1	2.4	<0.5	9.7	2.8	NT
2	1.4	< 0.5	7.3	1.8	NT
3	3.05	0.34	15.5	NT	NT
4	2.295	0.1014	10.3717	NT	NT
5	2.58	0.23	13.3	2.61	NT
6	2.31	<1	7.83	NT	NT
7	2	0.2	7.9	2.16	3.1
8	NS	NS	NS	NS	NS

Lab. Code	Atrazine	Diazinon	Dimethoate	Fenthion	Metsulfuron-methyl
9	2	<0.2	11	2.8	NT
10	2.34	0.24	8.25	3.1	4.43
11	NT	< 2	6.64	2.2	NT
12	0.85	<0.01	3.77	0.7	3.6
13	2.49	0.293	NT	4.1	3.17
14	2.3	< 0.1	6.58	2.98	< 2.5
15	2.15	0.18	14.7	2.72	1.46
16	2.5	<0.5	12.8	2.84	NT
17	2.27	0.20	13.95	NT	3.30
18	2.16	0.19	9.24	NT	3.49
19	1.94	0.241	10.1	3.13	NT
20	2.2	<0.2	9.1	2.7	3.2
21	2.3	0.2	NT	NT	4.04
22	1.57	0.21	8.8	NT	NT
23	2.9	0.27	8.9	3.1	4.2
24	NT	NT	NT	NT	NT
25	1.9	< 2	6.5	2.7	< 10
26	2.06	<0.5	9.40	3.37	NT
27	1.6	0.21	9.1	2.2	10
28	2.2	0.24	8.4	2.5	NT
29	1.9	0.16	11	2.3	2.3
30	2	<0.2	8.9	2.8	NT
31	NR	<2	19	2.9	NR
32	1.9296	0.1074	8.726	NT	NT
33	1.9322	0.1076	4.9502	NT	NT
34	NT	0.2	11.54	NT	NT
35	1.3	0.1	7.3	NT	1.7

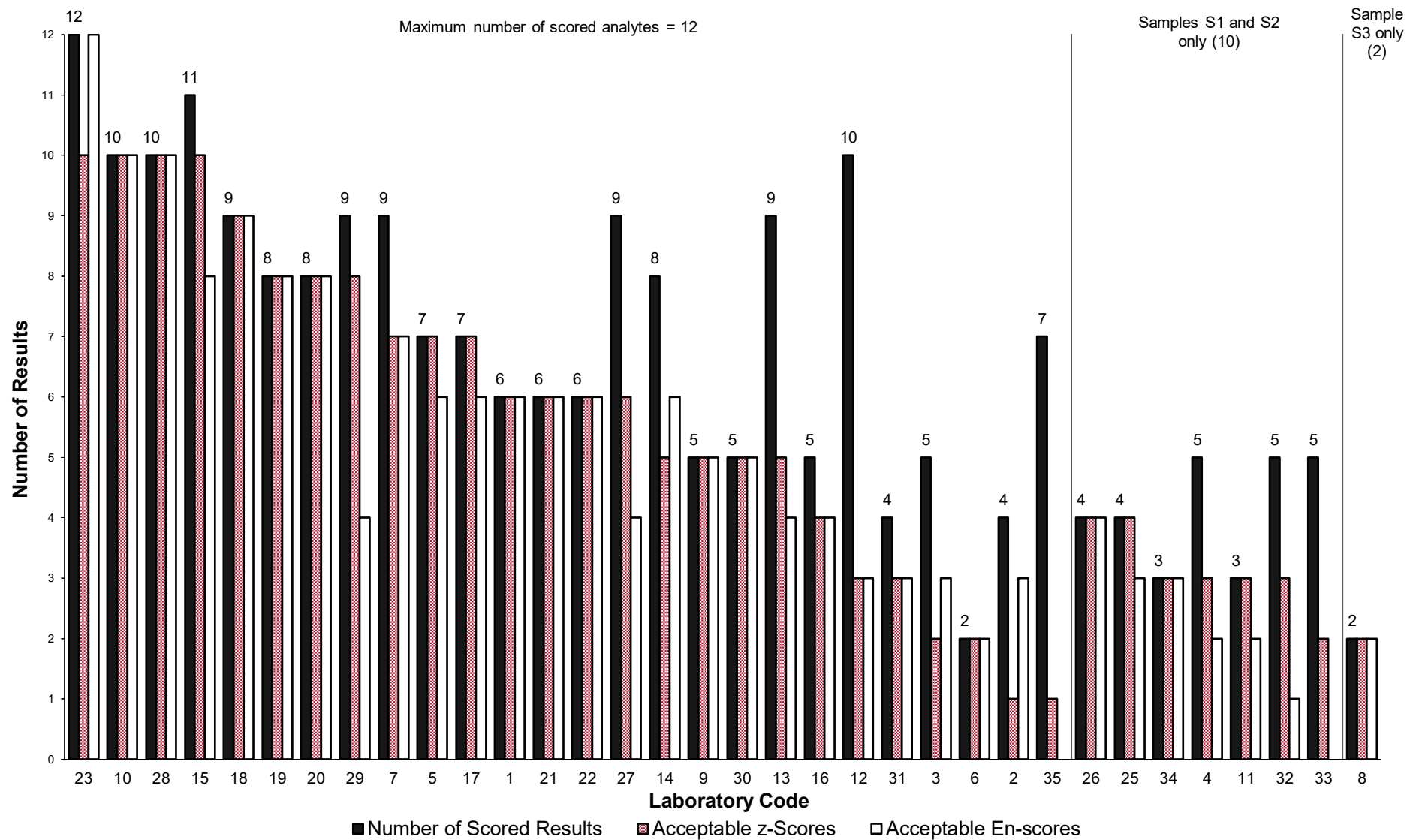
\*All values are in µg/L. Shaded cells are results which returned a questionable or unacceptable z-score for scored analytes. AV = Assigned Value, SV = Spiked Value.

Table 26 Summary of Participants' Results in Sample S3\*

Lab. Code	AMPA	Glyphosate
AV	7.4	3.06
SV	7.11	3.00
1	6.5	2.7
2	NT	NT
3	NT	NT
4	NS	NS
5	<30	<30

Lab. Code	AMPA	Glyphosate
6	NT	<10
7	NT	NT
8	6.82	3.29
9	NT	NT
10	7.71	3.1
11	NS	NS
12	19	8
13	NT	3.165
14	10.49	5.55
15	5.52	2.64
16	NT	NT
17	NT	NT
18	6.96	3.31
19	NT	2.75
20	<20	<10
21	7.3	3.5
22	NT	NT
23	7	3
24	NT	NT
25	NS	NS
26	NS	NS
27	NT	NT
28	7.0	3.1
29	NT	NT
30	NT	NT
31	10	<10
32	NS	NS
33	NS	NS
34	NS	NS
35	NS	NS

\*All values are in µg/L. Shaded cells are results which returned a questionable or unacceptable z-score for scored analytes.  
AV = Assigned Value, SV = Spiked Value.



Laboratory 24 did not report any numeric results for analytes of interest in this study.

Figure 33 Summary of Participants' Performance

### 6.11 Comparison with Previous Studies

A summary of participation and rates of reported results in NMIA Pesticides in River Water PT studies over the last ten studies (2015–2025) is presented in Figure 34.

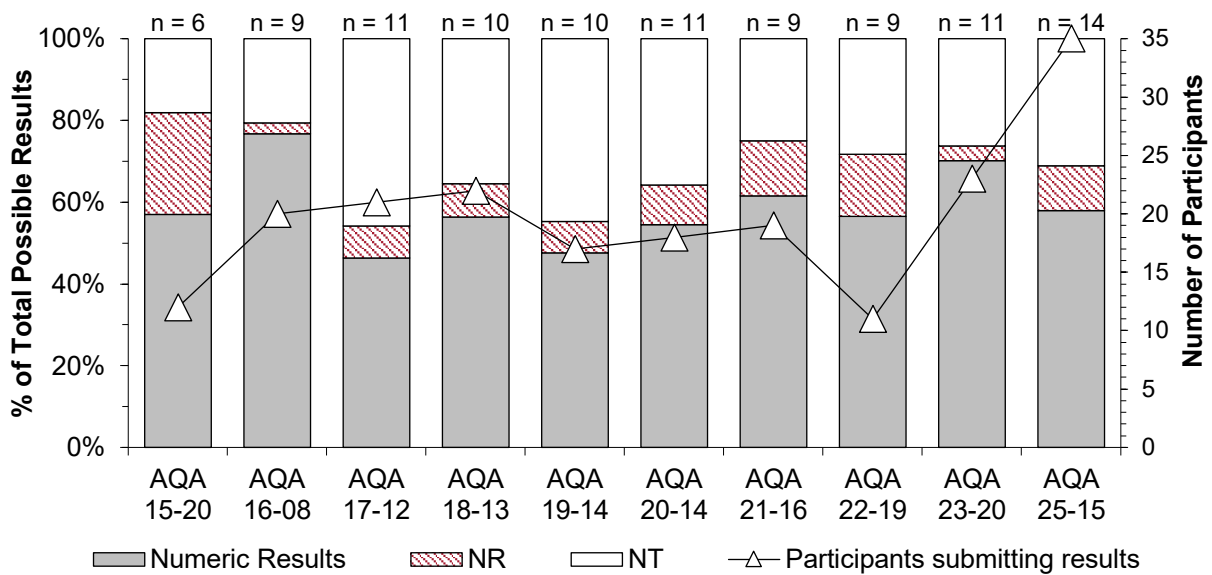


Figure 34 Summary of Participation and Reported Results in NMIA Pesticides in River Water PT Studies (n = number of spiked analytes)

A summary of the acceptable performance (presented as a percentage of the total number of scores for each study) in NMIA Pesticides in River Water PT studies over the last ten studies (2015–2025) is presented in Figure 35. To enable direct comparison, the SDPA used to calculate z-scores has been kept constant at 15% PCV. Over this period, the average proportion of acceptable scores was 80% for z-scores and 76% for  $E_n$ -scores.

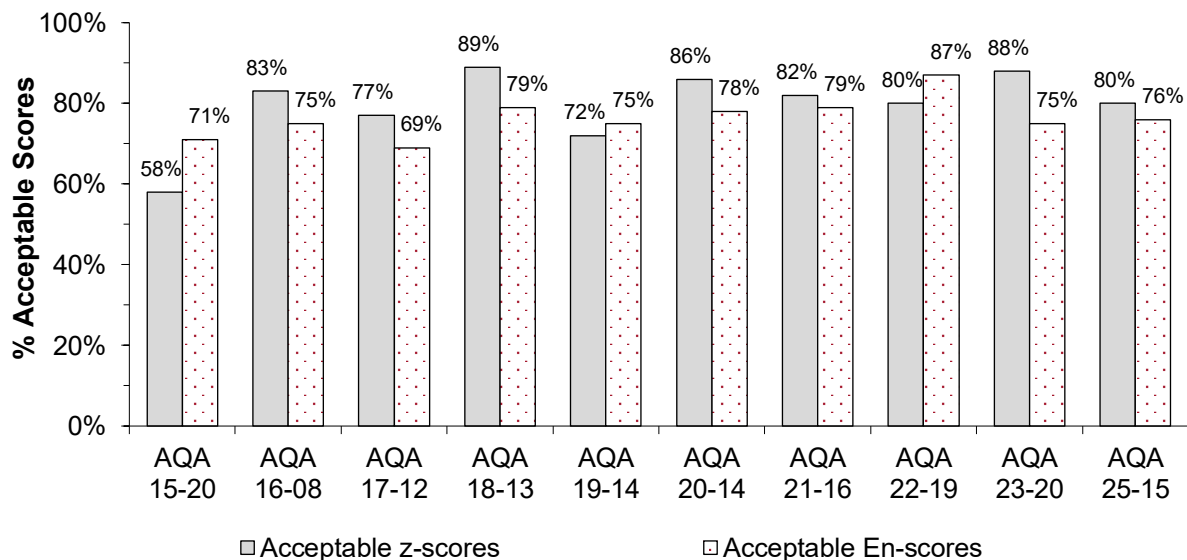


Figure 35 Acceptable z-Scores and  $E_n$ -Scores in NMIA Pesticides in River Water PT Studies

Individual performance history reports are emailed to participants at the end of each PT study; the consideration of z-scores over time provides much more useful information than a single z-score. Over time, laboratories should expect at least 95% of their z-scores to lie within the range  $|z| \leq 2.0$ . Scores in the range  $2.0 < |z| < 3.0$  can occasionally occur, however these should be interpreted in conjunction with the other scores obtained by that laboratory. For example, a trend of z-scores on one side of the zero line is an indication of laboratory bias.

As discussed in Section 6.2, it is a requirement of ISO/IEC 17025 that laboratories report their uncertainties.<sup>8</sup> Figure 36 presents a summary of the relative uncertainties as reported by participants over the last ten studies (2015–2025). Over this time period, the vast majority of numeric results were reported with uncertainties (96%), with 85% of participants reporting that they were accredited to ISO/IEC 17025.

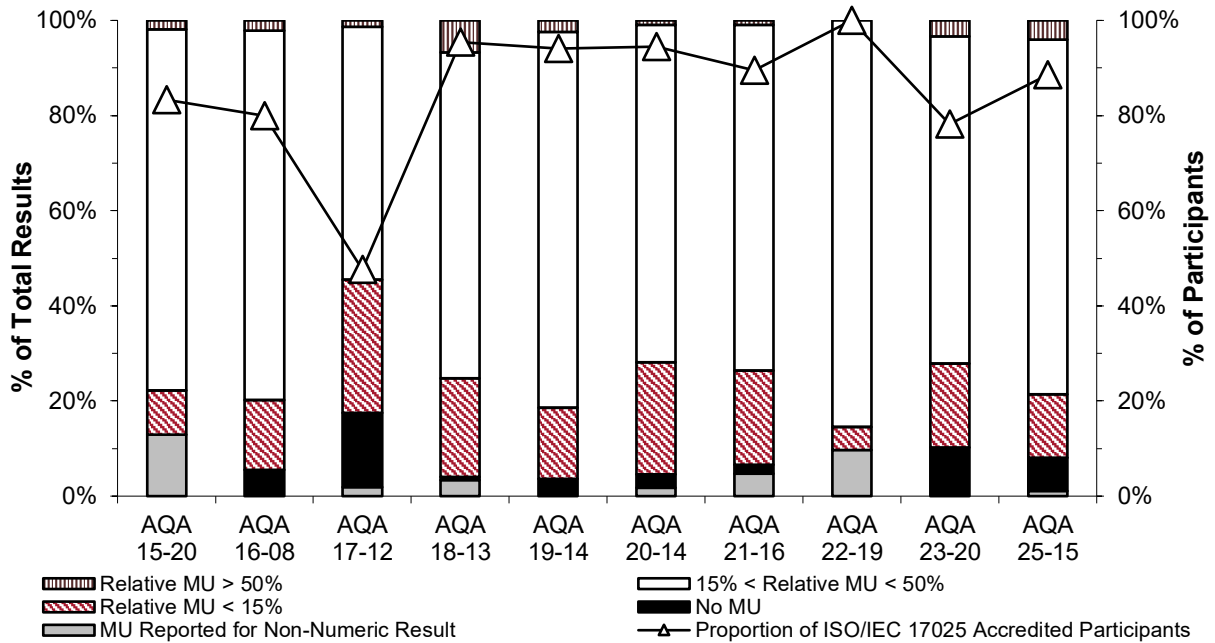


Figure 36 Summary of Participants' Relative Uncertainties for NMIA Pesticides in River Water PT Studies

## 7 REFERENCES

Please note that for all undated references, the latest edition of the referenced document (including any amendments) applies.

- [1] ISO/IEC 17043, *Conformity assessment – General requirements for the competence of proficiency testing providers*.
- [2] Commonwealth of Australia, Department of Industry, Science and Resources, NMIA, 2025, *Study Protocol for Proficiency Testing*, viewed December 2025, <[https://www.industry.gov.au/sites/default/files/2020-10/cpt\\_study\\_protocol.pdf](https://www.industry.gov.au/sites/default/files/2020-10/cpt_study_protocol.pdf)>
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- [5] National Environment Protection (Assessment of Site Contamination) Measure 1999 as amended 2013, Volume 2: Schedule B1, *Guideline on Investigation Levels for Soil and Groundwater*, viewed December 2025, <<https://www.legislation.gov.au/F2008B00713/latest/text/12>>
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- [7] Thompson, M., 2000, ‘Recent Trends in Inter-laboratory Precision at ppb and sub-ppb Concentrations in Relation to Fitness for Purpose Criteria in Proficiency Testing’, *Analyst*, vol 125, pp 385–386.
- [8] ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*.
- [9] Eurachem/CITAC Guide CG 4, QUAM:2012.P1, *Quantifying Uncertainty in Analytical Measurement*, 3<sup>rd</sup> ed., viewed December 2025, <[http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012\\_P1.pdf](http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf)>
- [10] BIPM, JCGM 200:2012, *International vocabulary of metrology – Basic and general concepts and associated terms (VIM)*, 3<sup>rd</sup> ed.

## **APPENDIX 1 SAMPLE PREPARATION**

The three samples were prepared using river water obtained from the Browns Waterhole. The water was filtered through a glass fibre filter and autoclaved.

The spiking solutions for Samples S1 and S2 were prepared by dissolving the standards in organic solvents. Glyphosate and AMPA for Sample S3 were dissolved in water.

The filtered, autoclaved water was dispensed into a stainless-steel pot. Each analyte was spiked into the water, and then stirred using a top-driven impeller stirrer for at least two hours.

Samples S1 and S2 were dispensed into 100 mL and 500 mL amber glass bottles. Sample S3 was dispensed into 500 mL PET bottles.

Between preparation and dispatch, the samples were stored in a coolroom at 4°C.

## APPENDIX 2 ASSESSMENT OF HOMOGENEITY AND STABILITY

### A2.1 Homogeneity

No homogeneity testing was performed for this study as the samples were prepared using a process previously demonstrated to produce sufficiently homogeneous samples. Participants' results in this study also gave no reason to question the samples' homogeneity.

### A2.2 Stability

No stability testing was conducted for this study, though previous use of these pesticides and similar analytes gave assurance that these samples were sufficiently stable. The samples were stored in a coolroom at 4 °C after preparation and prior to dispatch. For dispatch, the samples were packaged into insulated polystyrene foam boxes with cooler bricks.

Comparisons of results to days spend in transit for scored analytes in this study are presented in Figures 37 to 48 (solid blue lines are the assigned value  $\pm$  U). No significant analyte degradation with respect to the amount of time spent in transit was observed for scored analytes.

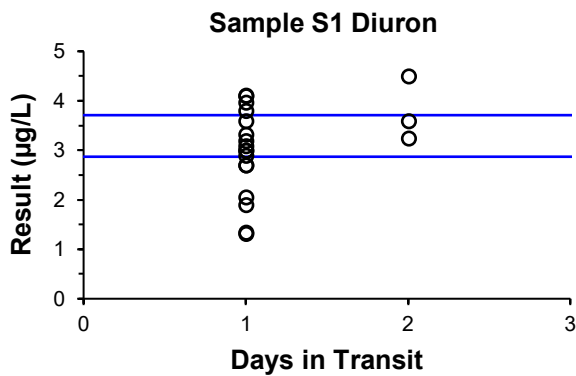


Figure 37 S1 Diuron Result vs Transit Days

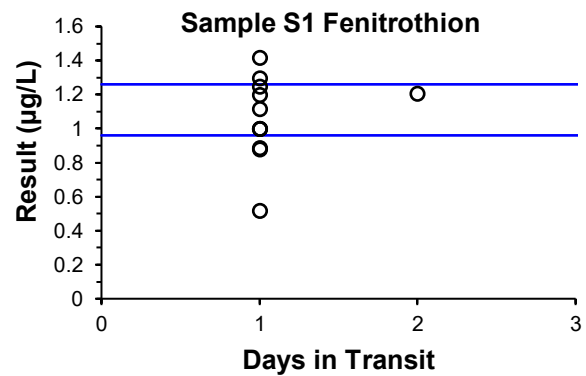


Figure 38 S1 Fenitrothion Result vs Transit Days

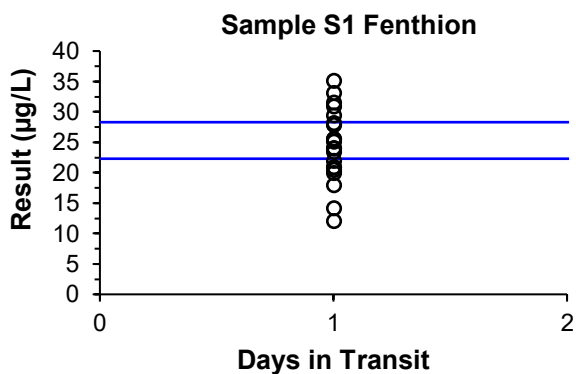


Figure 39 S1 Fenitrothion Result vs Transit Days

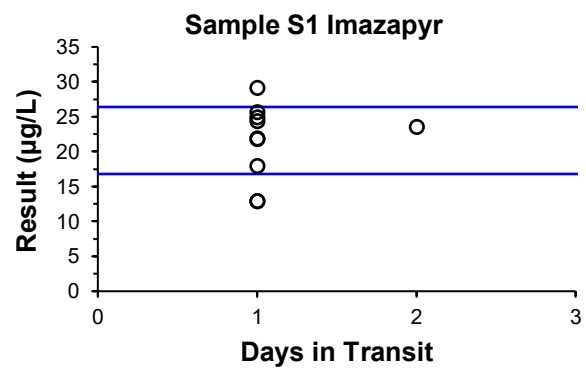


Figure 40 S1 Imazapyr Result vs Transit Days

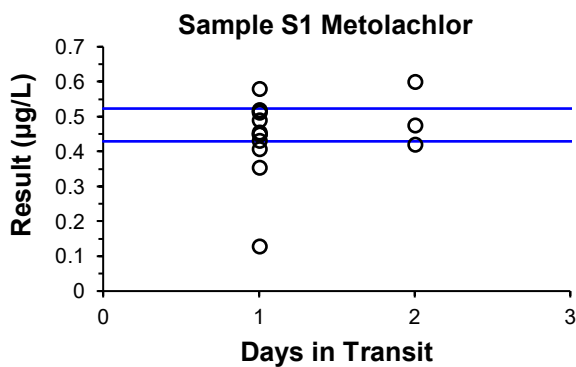


Figure 41 S1 Metolachlor Result vs Transit Days

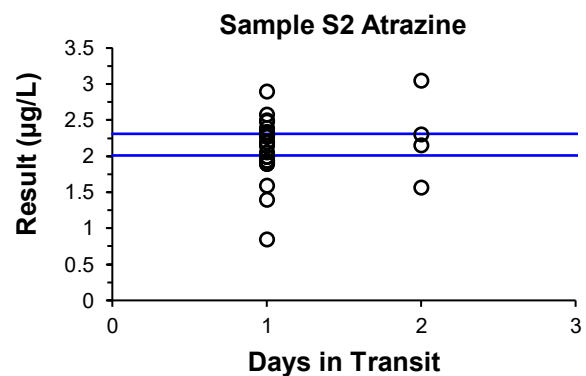


Figure 42 S2 Atrazine Result vs Transit Days

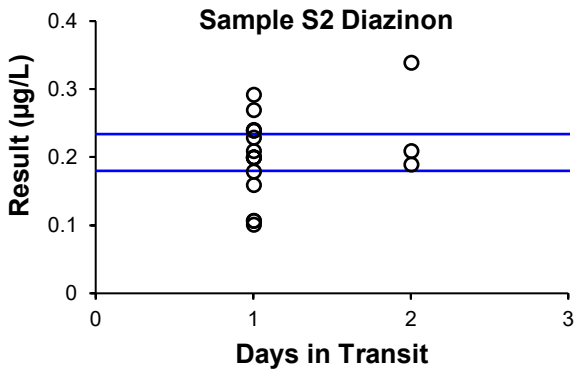


Figure 43 S2 Diazinon Result vs Transit Days

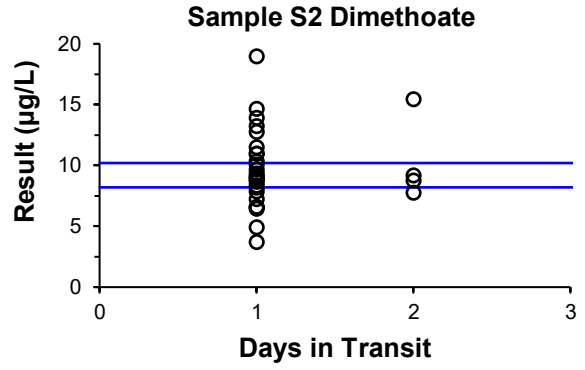


Figure 44 S2 Dimethoate Result vs Transit Days

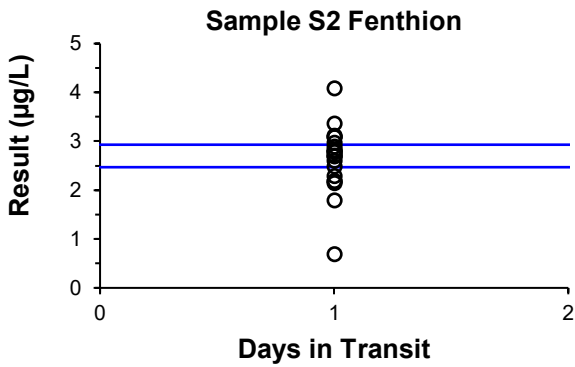


Figure 45 S2 Fenthion Result vs Transit Days

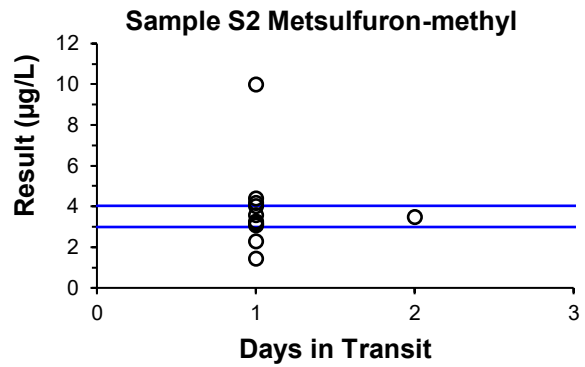


Figure 46 S2 Metsulfuron-methyl Result vs Transit Days

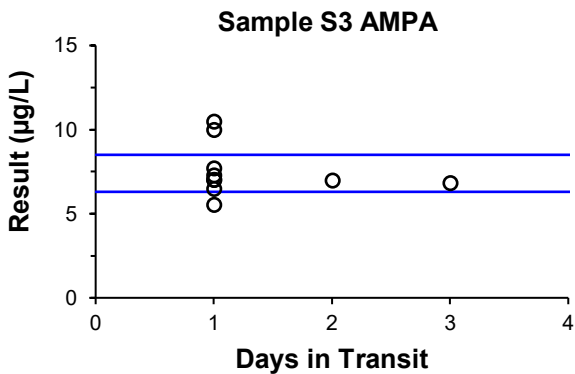


Figure 47 S3 AMPA Result vs Transit Days

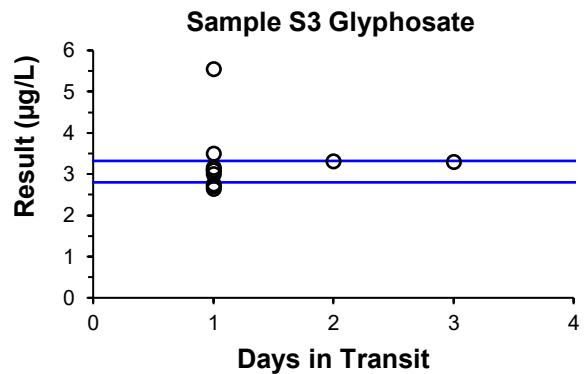


Figure 48 S3 Glyphosate Results vs Transit Days

## APPENDIX 3 ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY, z-SCORE AND E<sub>n</sub>-SCORE CALCULATIONS

### A3.1 Robust Average and Associated Uncertainty

Robust averages were calculated using the procedure described in ISO 13528.<sup>6</sup> The associated uncertainties were evaluated as according to Equation 4.

$$u_{rob\ av} = 1.25 \times \frac{S_{rob\ av}}{\sqrt{p}} \quad \text{Equation 4}$$

where:

$u_{rob\ av}$  is the standard uncertainty of the robust average

$S_{rob\ av}$  is the standard deviation of the robust average

$p$  is the number of results

The expanded uncertainty ( $U_{rob\ av}$ ) is the standard uncertainty multiplied by a coverage factor of 2 at approximately 95% confidence level.

A worked example is set out below in Table 27.

Table 27 Uncertainty of Robust Average for Fenthion in Sample S1

Number of results (p)	22
Robust Average	24.8 µg/L
$S_{rob\ av}$	5.9 µg/L
$u_{rob\ av}$	1.6 µg/L
$k$	2
$U_{rob\ av}$	3.2 µg/L

Therefore, the robust average for fenthion in Sample S1 is  $24.8 \pm 3.2$  µg/L.

### A3.2 z-Score and E<sub>n</sub>-Score Calculation

For each participant's result, a z-score and E<sub>n</sub>-score are calculated according to Equations 2 and 3 respectively (Section 4).

A worked example is set out below in Table 28.

Table 28 z-Score and E<sub>n</sub>-Score for Sample S2 Atrazine Result Reported by Laboratory 26

Participant Result (µg/L)	Assigned Value (µg/L)	SDPA	z-Score	E <sub>n</sub> -Score
2.06 ± 0.46	2.16 ± 0.15	15% as PCV, or: 0.15 × 2.16 = 0.324 µg/L	$z = \frac{2.06 - 2.16}{0.324}$ = -0.31	$E_n = \frac{2.06 - 2.16}{\sqrt{0.46^2 + 0.15^2}}$ = -0.21

#### APPENDIX 4 PARTICIPANTS' TEST METHODS

Participants were requested to provide information about their test methods. Responses are presented in Tables 29 to 42. Some responses may be modified so that the participant cannot be identified.

Table 29 Methodology – Aldrin

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
1	100	Yes	Liquid-Liquid	DCM	3 x 6 mL	30	85	5	N/A	GC-MS
3	40	No	Liquid-Liquid	Hexane	3 x 5 mL	NA	30	NA	NA	GC-MS/MS
4	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
5	30	No	Liquid-Liquid	DCM	1 x 1.5mL	90	N/A	N/A	Baked Sodium-Sulphate Column	GC-MS/MS
7	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS
8	NS									
9	100	Yes	Liquid-Liquid	DCM	3 x 10 mL	10	35	38	None	GC-MS/MS
10	50	N/A	Liquid-Liquid	Pentane:Hexane (20:80)	2 x 5 mL	30	30	30		GC-ECD
11	35	N/A	Liquid-Liquid	DCM	2 x 35 mL	30	45	30	None	GC-MS/MS
12	103mL	Yes	Liquid-Liquid	DCM	2x10mL	3	65	90		GC-MS/MS
14	35	No	Liquid-Liquid	DCM	1 x 2mL	10	21	10	None	GC-MS/MS
15	100	Yes	Liquid-Liquid	DCM	3 x 6 mL	6	50	20		GC-MS
16	100		Liquid-Liquid	DCM/HEX					NO	GC-ECD
18	500	Yes	SPE	DCM/ETOac	2x5 ml		40		None	GC-MS

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
20	100	Yes	Liquid-Liquid	DCM	3 x 10mL	10	35	45	none	GC-MS
21	100	No	Liquid-Liquid	Hexane	2 x 2 mL	2 x 2 min	NA	NA	None	GC-MS/MS
22	250	N/A	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5ml and step 3: 5mls	45mins in total	40	Not set	N/A	GC-ECD
23	470	Yes	Liquid-Liquid	DCM	150,100,50	10	40	20	none	GC-MS/MS
24	NT									
25	35	No	Liquid-Liquid	DCM	1 x 2mL	10	21	10	None	GC-MS/MS
26	100	Yes	Liquid-Liquid	DCM	3x6mL	12	55	17	N/A	GC-MS
27	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS
28	50	No	Liquid-Liquid	DCM	2X8mL	30	70		NA	GC-MS/MS
29	500	No	Liquid-Liquid	DCM	2 x 20 mL	10	none	none	none	GC-MS/MS
30	100	Yes	Liquid-Liquid	DCM	2 x 10 mL	3	42	40	None	GC-MS
31	35	N/A	Liquid-Liquid	DCM	2 x 2mL	10	35	3		GC-MS/MS
32	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
33	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
34	100	No	Liquid-Liquid	DCM	2 x 15 mL	10	35	30		GC-MS
35	100	Yes	Liquid-Liquid	DCM	3 x 6 mL	30	85	5	N/A	GC-MS

Table 30 Methodology – Diuron

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
3	20	No	QuEChERS	Acetonitrile	NA	NA	NA	NA	NA	LC-MS/MS
4	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
5	10	No	Direct Injection	N/A	N/A	10	N/A	N/A	Centrifugation	LC-MS/MS
7	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS
8	NS									
10	1	N/A	Direct Injection						Filtration	LC-MS/MS
12	1mL	N/A	Direct Injection	N/A	N/A	N/A	N/A	N/A	Filtration	LC-MS/MS
13	100	Yes	SPE	Methanol	2 x 4mL		40		None	LC-MS/MS
14	35	No	Liquid-Liquid	DCM	1 x 2mL	10	21	10	None	GC-MS/MS
15	100	Yes	Liquid-Liquid	DCM	3 x 6 mL	6	50	20		GC-MS
16	NT		NT	NT					NT	NT
17	2	N/A	Direct Injection							LC-MS/MS
18	10		Direct Injection						Filtration	LC-MS/MS
20	4	N/A	Direct Injection	N/A	N/A	N/A	N/A	N/A	none	LC-MS/MS

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
22	250	N/A	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5ml and step 3: 5mls	45mins in total	40	Not set	N/A	GC-MS
23	1	No	Direct Injection	water	1 X 1 mL	2	nil	nil	Filtration	LC-MS/MS
24	NT									
25	35	No	Liquid-Liquid	DCM	1 x 2mL	10	21	10	None	GC-MS/MS
26										
27	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS
28	50	No	Liquid-Liquid	DCM	2X8mL	30	70		NA	GC-MS/MS
29	1	No	Direct Injection	none	none	none	none	none	none	LC-MS/MS
31	35	N/A	Liquid-Liquid	DCM	2 x 2mL	10	35	3		GC-MS/MS
32	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
33	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
34	100	No	Liquid-Liquid	DCM	2 x 15 mL	10	35	30		GC-MS
35	1	No	Direct Injection	ACN co-solvent					Filtration	LC-MS/MS

Table 31 Methodology – Fenitrothion

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
4	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
5	10	No	Direct Injection	N/A	N/A	10	N/A	N/A	Centrifugation	LC-MS/MS
7	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS
8	NS									
9	100	Yes	Liquid-Liquid	DCM	3 x 10 mL	10	35	38	None	GC-MS/MS
10	1	N/A	Direct Injection						Filtration	LC-MS/MS
11	35	N/A	Liquid-Liquid	DCM	2 x 35 mL	30	45	30	None	GC-MS/MS
12	103mL	Yes	Liquid-Liquid	DCM	2x10mL	3	65	90		GC-MS/MS
14	35	No	Liquid-Liquid	DCM	1 x 2mL	10	21	10	None	GC-MS/MS
15	100	Yes	Liquid-Liquid	DCM	3 x 6 mL	6	50	20		GC-MS
16	100		Liquid-Liquid	DCM					NO	GC-MS
20	100	Yes	Liquid-Liquid	DCM	3 x 10mL	10	35	45	none	GC-MS
21	100	No	SPE	Acetone	2mL	NA	NA	NA	Filtration	GC-MS/MS
22	250	N/A	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5ml and step 3: 5mls	45mins in total	40	Not set	N/A	GC-MS
23	470	Yes	Liquid-Liquid	DCM	150,100,50	10	40	20	none	GC-MS/MS
24	NT									
25	35	No	Liquid-Liquid	DCM	1 x 2mL	10	21	10	None	GC-MS/MS

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
27	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS
28	50	No	Liquid-Liquid	DCM	2X8mL	30	70		NA	GC-MS/MS
29	1	No	Direct Injection	none	none	none	none	none	none	LC-MS/MS
30	100	Yes	Liquid-Liquid	DCM	2 x 10 mL	3	42	40	None	GC-MS
31	35	N/A	Liquid-Liquid	DCM	2 x 2mL	10	35	3		GC-MS/MS
32	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
33	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
34	100	No	Liquid-Liquid	DCM	2 x 15 mL	10	35	30		GC-MS

Table 32 Methodology – Fenthion

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
1	100	Yes	Liquid-Liquid	DCM	3 x 6 mL	30	85	5	N/A	GC-MS
4	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
5	10	No	Direct Injection	N/A	N/A	10	N/A	N/A	Centrifugation	LC-MS/MS
7	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS
8	NS									
9	100	Yes	Liquid-Liquid	DCM	3 x 10 mL	10	35	38	None	GC-MS/MS

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
10	1	N/A	Direct Injection						Filtration	LC-MS/MS
11	35	N/A	Liquid-Liquid	DCM	2 x 35 mL	30	45	30	None	GC-MS/MS
12	103mL	Yes	Liquid-Liquid	DCM	2x10mL	3	65	90		GC-MS/MS
13	100	Yes	SPE	Methanol	2 x 4mL		40		None	LC-MS/MS
14	35	No	Liquid-Liquid	DCM	1 x 2mL	10	21	10	None	GC-MS/MS
15	100	Yes	Liquid-Liquid	DCM	3 x 6 mL	6	50	20		GC-MS
16	100		Liquid-Liquid	DCM					NO	GC-MS
20	100	Yes	Liquid-Liquid	DCM	3 x 10mL	10	35	45	none	GC-MS
23	470	Yes	Liquid-Liquid	DCM	150,100,50	10	40	20	none	GC-MS/MS
24	NT									
25	35	No	Liquid-Liquid	DCM	1 x 2mL	10	21	10	None	GC-MS/MS
26	100	Yes	Liquid-Liquid	DCM	3x6mL	12	55	17	N/A	GC-MS
27	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS
28	50	No	Liquid-Liquid	DCM	2X8mL	30	70		NA	GC-MS/MS
29	500	No	Liquid-Liquid	DCM	2 x 20 mL	10	none	none	none	GC-MS/MS
30	100	Yes	Liquid-Liquid	DCM	2 x 10 mL	3	42	40	None	GC-MS
31	35	N/A	Liquid-Liquid	DCM	2 x 2mL	10	35	3		GC-MS/MS
32	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
33	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS

Table 33 Methodology – Imazapyr

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
4	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
5	10	No	Direct Injection	N/A	N/A	10	N/A	N/A	Centrifugation	LC-MS/MS
7	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS
8	NS									
12	1mL	N/A	Direct Injection	N/A	N/A	N/A	N/A	N/A	Filtration	LC-MS/MS
13	100	Yes	SPE	Methanol	2 x 4mL		40		None	LC-MS/MS
14	100	No	Liquid-Liquid	DCM	3 x 50mL	3 x 2	70	30	None	GC ion Trap
15	100	Yes	Liquid-Liquid	DCM	3 x 6 mL	6	50	20		GC-MS
16	NT		NT	NT					NT	NT
17	2	N/A	Direct Injection							LC-MS/MS
18	10		Direct Injection						Filtration	LC-MS/MS
20	4	N/A	Direct Injection	N/A	N/A	N/A	N/A	N/A	none	LC-MS/MS
23	1	No	Direct Injection	water	1 X 1 mL	2	nil	nil	Filtration	LC-MS/MS
24	NT									

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
27	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS
29	1	No	Direct Injection	none	none	none	none	none	none	LC-MS/MS
31	35	N/A	Liquid-Liquid	DCM	2 x 2mL	10	35	3		GC-MS/MS
32	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
33	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
35	1	No	Direct Injection	ACN co-solvent					Filtration	LC-MS/MS

Table 34 Methodology – Metolachlor

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
3	20	No	QuEChERS	Acetonitrile	NA	NA	NA	NA	NA	LC-MS/MS
4	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
5	10	No	Direct Injection	N/A	N/A	10	N/A	N/A	Centrifugation	LC-MS/MS
7	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS
8	NS									
9	100	Yes	Liquid-Liquid	DCM	3 x 10 mL	10	35	38	None	GC-MS/MS
10	50	N/A	Liquid-Liquid	Pentane:Hexane (20:80)	2 x 5 mL	30	30	30		GC-ECD

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
12	103mL	Yes	Liquid-Liquid	DCM	2x10mL	3	65	90		GC-MS/MS
13	100	Yes	SPE	Methanol	2 x 4mL		40		None	LC-MS/MS
14	100	No	Liquid-Liquid	DCM	3 x 50mL	3 x 2	70	30	None	GC ion Trap
15	100	Yes	Liquid-Liquid	DCM	3 x 6 mL	6	50	20		GC-MS
16	NT		NT	NT					NT	NT
17	2	N/A	Direct Injection							LC-MS/MS
18	10		Direct Injection						Filtration	LC-MS/MS
20	100	Yes	Liquid-Liquid	DCM	3 x 10mL	10	35	45	none	GC-MS
22	250	N/A	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5ml and step 3: 5mls	45mins in total	40	Not set	N/A	GC-MS
23	1	No	Direct Injection	water	1 X 1 mL	2	nil	nil	Filtration	LC-MS/MS
24	NT									
25	100	No	Liquid-Liquid	DCM/Ether	3 x 30mL	3 x 10	70	30	None	HPLC DAD
27	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS
28	50	No	Liquid-Liquid	DCM	2X8mL	30	70		NA	GC-MS/MS
29	500	No	Liquid-Liquid	DCM	2 x 20 mL	10	none	none	none	GC-MS/MS
30	100	Yes	Liquid-Liquid	DCM	2 x 10 mL	3	42	40	None	GC-MS
31	35	N/A	Liquid-Liquid	DCM	2 x 2mL	10	35	3		GC-MS/MS
32	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
33	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
35	1	No	Direct Injection	ACN co-solvent					Filtration	LC-MS/MS

Table 35 Methodology – Atrazine

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
1	100	Yes	Liquid-Liquid	DCM	3 x 6 mL	30	85	5	N/A	GC-MS
3	20	No	QuEChERS	Acetonitrile	NA	NA	NA	NA	NA	LC-MS/MS
4	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
5	10	No	Direct Injection	N/A	N/A	10	N/A	N/A	Centrifugation	LC-MS/MS
7	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS
8	NS									
9	100	Yes	Liquid-Liquid	DCM	3 x 10 mL	10	35	38	None	GC-MS/MS
10	1	N/A	Direct Injection						Filtration	LC-MS/MS
12	103mL	Yes	Liquid-Liquid	DCM	2x10mL	3	65	90		GC-MS/MS
13	100	Yes	SPE	Methanol	2 x 4mL		40		None	LC-MS/MS
14	35	No	Liquid-Liquid	DCM	1 x 2mL	10	21	10	None	GC-MS/MS
15	100	Yes	Liquid-Liquid	DCM	3 x 6 mL	6	50	20		GC-MS
16	100		Liquid-Liquid	DCM					NO	GC-MS

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
17	2	N/A	Direct Injection							LC-MS/MS
18	10		Direct Injection						Filtration	LC-MS/MS
20	100	Yes	Liquid-Liquid	DCM	3 x 10mL	10	35	45	none	GC-MS
21	100	No	SPE	Acetone	2mL	NA	NA	NA	Filtration	GC-MS/MS
22	250	N/A	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5ml and step 3: 5mls	45mins in total	40	Not set	N/A	GC-MS
23	1	No	Direct Injection	water	1 X 1 mL	2	nil	nil	Filtration	LC-MS/MS
24	NT									
25	35	No	Liquid-Liquid	DCM	1 x 2mL	10	21	10	None	GC-MS/MS
26	100	Yes	Liquid-Liquid	DCM	3x6mL	12	55	17	N/A	GC-MS
27	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS
28	50	No	Liquid-Liquid	DCM	2X8mL	30	70		NA	GC-MS/MS
29	500	No	Liquid-Liquid	DCM	2 x 20 mL	10	none	none	none	GC-MS/MS
30	100	Yes	Liquid-Liquid	DCM	2 x 10 mL	3	42	40	None	GC-MS
31	35	N/A	Liquid-Liquid	DCM	2 x 2mL	10	35	3		GC-MS/MS
32	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
33	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
35	1	No	Direct Injection	ACN co-solvent					Filtration	LC-MS/MS

Table 36 Methodology – Deltamethrin

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
3	20	No	QuEChERS	Acetonitrile	NA	NA	NA	NA	NA	LC-MS/MS
4	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
5	30	No	Liquid-Liquid	DCM	1 x 1.5mL	90	N/A	N/A	Baked Sodium-Sulphate Column	GC-MS/MS
7	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS
8	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
9	100	Yes	Liquid-Liquid	DCM	3 x 10 mL	10	35	38	None	GC-MS/MS
12	103mL	Yes	Liquid-Liquid	DCM	2x10mL	3	65	90		GC-MS/MS
14	35	No	Liquid-Liquid	DCM	2 x 2mL	10	21	10	None	GC-MS/MS
16	100		Liquid-Liquid	DCM					NO	GC-MS
18	500	Yes	SPE	DCM/ETOac	2x5 ml		40		None	GC-MS
20	100	Yes	Liquid-Liquid	DCM	3 x 10mL	10	35	45	none	GC-MS
22	250	N/A	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5ml and step 3: 5mls	45mins in total	40	Not set	N/A	GC-MS
23	470	Yes	Liquid-Liquid	DCM	150,100,50	10	40	20	none	GC-MS/MS
24	NT									
27	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
28	50	No	Liquid-Liquid	DCM	2X8mL	30	70		NA	GC-MS/MS
29	500	No	Liquid-Liquid	DCM	2 x 20 mL	10	none	none	none	GC-MS/MS
30	100	Yes	Liquid-Liquid	DCM	2 x 10 mL	3	42	40	None	GC-MS
31	35	N/A	Liquid-Liquid	DCM	2 x 2mL	10	35	3		GC-MS/MS
32	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
33	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS

Table 37 Methodology – Diazinon

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
1	100	Yes	Liquid-Liquid	DCM	3 x 6 mL	30	85	5	N/A	GC-MS
3	20	No	QuEChERS	Acetonitrile	NA	NA	NA	NA	NA	LC-MS/MS
4	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
5	10	No	Direct Injection	N/A	N/A	10	N/A	N/A	Centrifugation	LC-MS/MS
7	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS
8	NS									
9	100	Yes	Liquid-Liquid	DCM	3 x 10 mL	10	35	38	None	GC-MS/MS
10	1	N/A	Direct Injection						Filtration	LC-MS/MS
11	35	N/A	Liquid-Liquid	DCM	2 x 35 mL	30	45	30	None	GC-MS/MS

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
12	103mL	Yes	Liquid-Liquid	DCM	2x10mL	3	65	90		GC-MS/MS
13	100	Yes	SPE	Methanol	2 x 4mL		40		None	LC-MS/MS
14	35	No	Liquid-Liquid	DCM	1 x 2mL	10	21	10	None	GC-MS/MS
15	100	Yes	Liquid-Liquid	DCM	3 x 6 mL	6	50	20		GC-MS
16	100		Liquid-Liquid	DCM					NO	GC-MS
17	2	N/A	Direct Injection							LC-MS/MS
18	500	Yes	SPE	DCM/ETOcc	2x5 ml		40		None	GC-MS
20	100	Yes	Liquid-Liquid	DCM	3 x 10mL	10	35	45	none	GC-MS
21	100	No	SPE	Acetone	2mL	NA	NA	NA	Filtration	GC-MS/MS
22	250	N/A	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5ml and step 3: 5mls	45mins in total	40	Not set	N/A	GC-MS
23	1	No	Direct Injection	water	1 X 1 mL	2	nil	nil	Filtration	LC-MS/MS
24	NT									
25	35	No	Liquid-Liquid	DCM	1 x 2mL	10	21	10	None	GC-MS/MS
26	100	Yes	Liquid-Liquid	DCM	3x6mL	12	55	17	N/A	GC-MS
27	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS
28	50	No	Liquid-Liquid	DCM	2X8mL	30	70		NA	GC-MS/MS
29	500	No	Liquid-Liquid	DCM	2 x 20 mL	10	none	none	none	GC-MS/MS
30	100	Yes	Liquid-Liquid	DCM	2 x 10 mL	3	42	40	None	GC-MS

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
31	35	N/A	Liquid-Liquid	DCM	2 x 2mL	10	35	3		GC-MS/MS
32	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
33	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
34	100	No	Liquid-Liquid	DCM	2 x 15 mL	10	35	30		GC-MS
35	1	No	Direct Injection	ACN co-solvent					Filtration	LC-MS/MS

Table 38 Methodology – Dimethoate

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
1	100	Yes	Liquid-Liquid	DCM	3 x 6 mL	30	85	5	N/A	GC-MS
3	20	No	QuEChERS	Acetonitrile	NA	NA	NA	NA	NA	LC-MS/MS
4	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
5	10	No	Direct Injection	N/A	N/A	10	N/A	N/A	Centrifugation	LC-MS/MS
7	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS
8	NS									
9	100	Yes	Liquid-Liquid	DCM	3 x 10 mL	10	35	38	None	GC-MS/MS
10	1	N/A	Direct Injection						Filtration	LC-MS/MS
11	35	N/A	Liquid-Liquid	DCM	2 x 35 mL	30	45	30	None	GC-MS/MS

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
12	103mL	Yes	Liquid-Liquid	DCM	2x10mL	3	65	90		GC-MS/MS
14	35	No	Liquid-Liquid	DCM	1 x 2mL	10	21	10	None	GC-MS/MS
15	100	Yes	Liquid-Liquid	DCM	3 x 6 mL	6	50	20		GC-MS
16	100		Liquid-Liquid	DCM					NO	GC-MS
17	2	N/A	Direct Injection							LC-MS/MS
18	10		Direct Injection						Filtration	LC-MS/MS
20	100	Yes	Liquid-Liquid	DCM	3 x 10mL	10	35	45	none	GC-MS
22	250	N/A	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5ml and step 3: 5mls	45mins in total	40	Not set	N/A	GC-MS
23	1	No	Direct Injection	water	1 X 1 mL	2	nil	nil	Filtration	LC-MS/MS
24	NT									
25	35	No	Liquid-Liquid	DCM	1 x 2mL	10	21	10	None	GC-MS/MS
26	100	Yes	Liquid-Liquid	DCM	3x6mL	12	55	17	N/A	GC-MS
27	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS
28	50	No	Liquid-Liquid	DCM	2X8mL	30	70		NA	GC-MS/MS
29	1	No	Direct Injection	none	none	none	none	none	none	LC-MS/MS
30	100	Yes	Liquid-Liquid	DCM	2 x 10 mL	3	42	40	None	GC-MS
31	35	N/A	Liquid-Liquid	DCM	2 x 2mL	10	35	3		GC-MS/MS

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
32	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
33	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
34	100	No	Liquid-Liquid	DCM	2 x 15 mL	10	35	30		GC-MS
35	1	No	Direct Injection	ACN co-solvent					Filtration	LC-MS/MS

Table 39 Methodology – Metsulfuron-methyl

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
4	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
7	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS
8	NS									
10	1	N/A	Direct Injection						Filtration	LC-MS/MS
12	1mL	N/A	Direct Injection	N/A	N/A	N/A	N/A	N/A	Filtration	LC-MS/MS
13	100	Yes	SPE	Methanol	2 x 4mL		40		None	LC-MS/MS
14	100	No	Liquid-Liquid	DCM	3 x 50mL	3 x 2	70	30	None	GC ion Trap
15	206	No	Direct Injection	NA	1 x 1mL	6	NA	NA	Filtration	LC-MS
16	NT		NT	NT					NT	NT

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Technique
17	2	N/A	Direct Injection							LC-MS/MS
18	10		Direct Injection						Filtration	LC-MS/MS
20	4	N/A	Direct Injection	N/A	N/A	N/A	N/A	N/A	none	LC-MS/MS
21	1	No	Direct Injection	N/A	1				Filtration	LC-MS/MS
23	1	No	Direct Injection	water	1 X 1 mL	2	nil	nil	Filtration	LC-MS/MS
24	NT									
25	100	No	Liquid-Liquid	DCM/Ether	3 x 30mL	3 x 10	70	30	None	HPLC DAD
27	100	N/A	SPE	MeOH & ACN:DCM 1:1 Solution	2 mL & 3 x 10 mL	N/A	55 & 45	N/A	Filtration	LC-HRMS & GC-MS/MS
29	1	No	Direct Injection	none	none	none	none	none	none	LC-MS/MS
31	35	N/A	Liquid-Liquid	DCM	2 x 2mL	10	35	3		GC-MS/MS
32	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
33	500	Yes	SPE	DCM/EtOAc	25mL, 10 steps	25	35	25	Filtration	GC-MS
35	1	No	Direct Injection	ACN co-solvent					Filtration	LC-MS/MS

Table 40 Methodology – AMPA

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Derivatisation Procedure	Derivatisation Agent	Measurement Technique
1	1	N/A	Direct Injection			LC-MS/MS
3	NT					
4	NS					
5	5	No	Liquid-Liquid	Pre-column	9-fluorenyl-methylchloroformate in acetone	HPLC
8	0.1	N/A	NA	Pre-instrument	MeOH/Acetic Anhydride	LC-MS/MS
9	NT					
10	1	N/A	Direct Injection	Pre-column	FMOC	LC-MS/MS
11	NS					
12	0.5mL	N/A	Direct Injection	Pre-column	9-Fluorenylmethoxycarbonyl chloride	LC-MS/MS
14	1	N/A	Direct Injection	Pre-column	FMOC	LC-MS/MS
15	5	No	Direct Injection	Pre-column	FMOC	LC-MS/MS
16	NT					
18	10		Direct Injection	Underivatised		LC-MS/MS
20	4mL	N/A	Direct Injection	Pre-column	9-Fluorenylmethoxy carbonyl chloride	LC-MS/MS
21	0.4	No	Direct Injection	Pre-column	FMOC	LC-FLD
23	0.5	No	Direct Injection	N/A	N/A	LC-MS/MS
24	NT					
25	NS					
26	NS					
28	5	No	Liquid-Liquid		FMOC	LC-MS/MS
31	1		Direct Injection			LC-MS/MS

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Derivatisation Procedure	Derivatisation Agent	Measurement Technique
32				NS		
33				NS		
34				NS		
35				NS		

Table 41 Methodology – Glyphosate

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Derivatisation Procedure	Derivatisation Agent	Measurement Technique
1	1	N/A	Direct Injection			LC-MS/MS
3	NT					
4				NS		
5	5	No	Liquid-Liquid	Pre-column	9-fluorenyl-methylchloroformate in acetone	HPLC
8	0.1	N/A	NA	Pre-instrument	MeOH/Acetic Anhydride	LC-MS/MS
9	NT					
10	1	N/A	Direct Injection	Pre-column	FMOc	LC-MS/MS
11				NS		
12	0.5mL	N/A	Direct Injection	Pre-column	9-Fluorenylmethoxycarbonyl chloride	LC-MS/MS
13	1		Direct Injection	None		LC-MS/MS
14	1	N/A	Direct Injection	Pre-column	FMOc	LC-MS/MS
15	5	No	Direct Injection	Pre-column	FMOc	LC-MS/MS
16				NT		
18	10		Direct Injection	Underivatised		LC-MS/MS

Lab. Code	Sample Volume (mL)	Was the container rinsed?	Extraction Technique	Derivatisation Procedure	Derivatisation Agent	Measurement Technique
20	4mL	N/A	Direct Injection	Pre-column	9-Fluorenylmethyloxycarbonyl chloride	LC-MS/MS
21	0.4	No	Direct Injection	Pre-column	Fmoc	LC-FLD
23	0.5	No	Direct Injection	N/A	N/A	LC-MS/MS
24	NT					
25	NS					
26	NS					
28	5	No	Liquid-Liquid		Fmoc	LC-MS/MS
31	1		Direct Injection			LC-MS/MS
32	NS					
33	NS					
34	NS					
35	NS					

Table 42 Methodology – Additional Comments

Lab. Code	Sample	Participant's Comments
13	S1	Recoveries of dichlorvos, malathion and imazapyr are based on recovery of spiked sample. All other reported recoveries are based on recovery of labelled internal standards. NR - no result due to poor recovery in spiked samples (less than 10%)
18	S2	Deltamethrin in samples seems to be a mixture of isomers. We only reported the one in our calibration standard which is specifically only the active isomer of deltamethrin.
21	All	S1/S2 - Acidic Herbicides analysed on 08/09/2025 S3 - Glyphosate/AMPA analysed 09/09/2025 (not accredited) S1/S2 - Triazine & OP Pesticides analysed on 17/09/2025. S1/S2 OC Pesticides analysed on 22/09/2025

## APPENDIX 5 ACRONYMS AND ABBREVIATIONS

Ace	Acetone
Ac <sub>2</sub> O	Acetic Anhydride
ACN	Acetonitrile
AMPA	Aminomethylphosphonic acid
AV	Assigned Value
Centr.	Centrifugation
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
2,4-D	2,4-Dichlorophenoxyacetic acid
DAD	Diode Array Detection
DCM	Dichloromethane
DI	Direct Injection
ECD	Electron Capture Detection
EtOAc	Ethyl Acetate
Filtr.	Filtration
FLD	Fluorescence Detection
Fmoc	Fluorenylmethyloxycarbonyl
GC	Gas Chromatography
GUM	Guide to the expression of Uncertainty in Measurement
Hex	Hexane
HPLC	High Performance Liquid Chromatography
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
LC	Liquid Chromatography
LLE	Liquid-Liquid Extraction
LOR	Limit of Reporting
Max	Maximum
MCPA	2-methyl-4-chlorophenoxyacetic acid
Md	Median
MeOH	Methanol
Min	Minimum
MS	Mass Spectrometry
MS/MS	Tandem Mass Spectrometry

MU	Measurement Uncertainty
N	Number of numeric results
NA	Not Applicable
NATA	National Association of Testing Authorities, Australia
NMIA	National Measurement Institute, Australia
NR	Not Reported
NS	Not Supplied
NT	Not Tested
<i>p,p'</i> -DDD	Dichlorodiphenyldichloroethane
<i>p,p'</i> -DDE	Dichlorodiphenyldichloroethylene
<i>p,p'</i> -DDT	Dichlorodiphenyltrichloroethane
PCV	Performance Coefficient of Variation
Pent	Pentane
PT	Proficiency Testing
QuEChERS	Quick, Easy, Cheap, Effective, Rugged and Safe extraction method
RA	Robust Average
Rec	Recovery
RM	Reference Material
SD	Standard Deviation
SDPA	Standard Deviation for Proficiency Assessment
SI	International System of Units
SPE	Solid Phase Extraction
SS	Spiked Samples
SV	Spiked Value (or formulated concentration of a PT sample)
Total DDT	Total amount of DDD, DDE and DDT
U	Expanded Uncertainty

**END OF REPORT**