Australian Government
Department of Industry, Science, Energy and Resources

National Measurement Institute

# Proficiency Test Final Report
# AQA 21-03
# Pesticides in Soil

July 2021

## ACKNOWLEDGMENTS

This study was conducted by the National Measurement Institute (NMI). Support funding was provided by the Australian Government Department of Industry, Science, Energy and Resources.

I would like to thank the management and staff of the participating laboratories for supporting the study. It is only through widespread participation that we can provide an effective service to laboratories.

The assistance of the following NMI staff members in the planning, conduct and reporting of the study is acknowledged.

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## SUMMARY

AQA 21-03 Pesticides in Soil commenced in March 2021. Twenty-four laboratories enrolled to participate, and twenty-two participants submitted results.

Two soil samples were prepared using soil bought from a Sydney supplier. Sample S1 was prepared by spiking the soil with bifenthrin, cyfluthrin, dieldrin and glyphosate. Sample S2 was prepared by spiking the soil with p,p'-DDE, *trans*-chlordane and imidacloprid.

Of a possible 154 numeric results, a total of 84 numeric results (55%) were submitted. Twelve results were submitted as a 'less than' value (<*x*) or Not Reported (NR), and 58 results were submitted as Not Tested (NT).

The assigned values for all scored analytes were the robust averages of participants' results. The associated uncertainties were estimated 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 ability of participants to correctly identify environmentally significant pesticides in soil.*

Laboratories **14**, **17** and **22** reported results for all scored analytes.

Four laboratories did not report results for analytes that they tested for and that were spiked into the test samples (total of four results). Three laboratories reported analytes that were not spiked into the test samples (total of three results).

- *Compare the performances of participants and assess their accuracy in the measurement of pesticides in soil.*

Of 73 z-scores, 63 (86%) returned $|z| \leq 2.0$, indicating a satisfactory performance. Laboratory **22** returned satisfactory z-scores for all scored analytes.

Of 73 $E_n$-scores, 63 (86%) returned $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective uncertainties.

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

Participants used a wide variety of methods; no correlation with results was evident.

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

All numeric results were reported with an associated estimate of uncertainty. The magnitude of these expanded uncertainties ranged from 8.5% to 160000% of the reported value.

- *Compare the performance of participants with past performance.*

Taken as a group, the performance for participants in pesticides in soil studies has been improving over the last few studies.

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

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

# 1 INTRODUCTION

## 1.1 NMI Proficiency Testing Program

The National Measurement Institute (NMI) 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 inter-laboratory comparison'.[1] NMI PT studies target chemical testing in areas of high public significance such as trade, environment, law enforcement and food safety. NMI offers studies in:

- pesticide residues in fruit and vegetables, soil and water;
- petroleum hydrocarbons in soil and water;
- inorganic analytes in soil, water, filters, food and pharmaceuticals;
- controlled drug assay, drugs in wipes and clandestine laboratory;
- PFAS in water, soil, biota and food; and
- allergens in food.

## 1.2 Study Aims

The aims of the study were to:

- assess the ability of participants to correctly identify environmentally significant pesticides in soil;
- compare the performances of participants and assess their accuracy in the measurement of pesticides in soil;
- evaluate participants' methods for the measurement of pesticides in soil;
- develop the practical application of traceability and measurement uncertainty, and provide participants with information that will be useful in assessing their uncertainty estimates;
- compare the performance of participants with past performance; 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 NMI proficiency tests is described in the NMI Study Protocol for Proficiency Testing.[2] The statistical methods used are described in the NMI Chemical Proficiency Testing Statistical Manual.[3] These documents have been prepared with reference to ISO/IEC 17043 and The International Harmonized Protocol for The Proficiency Testing of Analytical Chemistry Laboratories.[1,4]

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

## 2 STUDY INFORMATION

### 2.1 Selection of Pesticides

A list of possible analytes spiked into Samples S1 and S2 is presented in Table 1.

Table 1 List of Possible Analytes

| | | |
|---|---|---|
| Aldrin | p,p'-DDT | Heptachlor epoxide |
| Atrazine | Total DDT | Hexachlorobenzene |
| Bifenthrin | Dieldrin | Imidacloprid |
| *cis*-Chlordane | Diuron | Lindane |
| *trans*-Chlordane | alpha-Endosulfan | Malathion |
| Total Chlordane | beta-Endosulfan | MCPA |
| Chlorpyrifos | Endosulfan sulfate | Metsulfuron-methyl |
| Cyfluthrin | Ethion | Parathion |
| Cypermethrin | Fenitrothion | Parathion-methyl |
| 2,4-D | Fenthion | Permethrin |
| Diazinon | Fenvalerate | Simazine |
| Dicamba | Fipronil | Tebuconazole |
| p,p'-DDD | Glyphosate | Triclopyr |
| p,p'-DDE | Heptachlor | Trifluralin |

The actual spiked pesticides for Samples S1 and S2 are presented in Table 2. The pesticides and spiked values used in this study were selected with consideration to:

- a variety of pesticides, including some amenable to both gas chromatography and liquid chromatography; and
- the National Environmental Protection (Assessment of Site Contamination) Measure Schedule B1 *Guideline on Investigation Levels for Soil and Groundwater*.[5]

Table 2 Spiked Values of Test Samples

| Sample | Analyte | Spiked Value (mg/kg) | Uncertainty (mg/kg)* |
|---|---|---|---|
| S1 | Bifenthrin | 0.0259 | 0.0013 |
| | Cyfluthrin | 0.0195 | 0.0010 |
| | Dieldrin | 1.20 | 0.06 |
| | Glyphosate | 1.30 | 0.07 |
| S2 | p,p’-DDE | 0.604 | 0.030 |
| | *trans*-Chlordane | 0.555 | 0.028 |
| | Imidacloprid | 0.151 | 0.008 |

* The uncertainty is an expanded uncertainty at approximately 95% confidence using a coverage factor of 2. It has been estimated with consideration to contributions from the gravimetric and volumetric operations involved in spiking the samples, and the purity of the pesticide reference standards. Stability was not considered in the uncertainty budget and so the expanded uncertainty relates to the mass fraction of analyte at the time of spiking.

### 2.2 Study Timetable

The timetable of the study was:

| | |
|---|---|
| Invitation issued | 4 March 2021 |
| Samples dispatched | 6 April 2021 |
| Results due | 17 May 2021 |
| Interim report issued | 20 May 2021 |

### 2.3 Participation and Laboratory Code

Twenty-four laboratories enrolled to participate in this study, and all participants were assigned a confidential laboratory code number. Twenty-two participants submitted results.

### 2.4 Sample Preparation

Two soil samples were prepared by spiking soil purchased from a Sydney supplier with various pesticides to obtain the mass fractions listed in Table 2. The preparation of the samples is described in Appendix 1.

### 2.5 Homogeneity of Samples

The samples were prepared and packaged using a process that has been demonstrated to produce homogeneous samples from previous NMI Pesticides in Soil PT studies. No homogeneity testing was conducted for this study, and the participants' results gave no reason to question the homogeneity of the samples.

### 2.6 Stability of Analytes

No assessment of the stability of the pesticides was made before the samples were sent. To assess possible instability, the results returned by participants were compared to the spiked values. Robust averages of participants' results were within 74 – 80% of the spiked values for scored analytes. This provides good support for the stability of these analytes in the test samples and similar ratios have been observed in previous NMI Pesticides in Soil PT studies (as presented in PT Report AQA 16-04 Pesticides in Soil).[6] A transportation stability assessment was also made for all scored analytes (Appendix 2).

### 2.7 Sample Storage, Dispatch and Receipt

The test samples were refrigerated at 4 °C prior to dispatch. Participants were sent one 50 g jar of spiked soil for each of Samples S1 and S2. The samples were packed in a foam box with cooler bricks and sent by courier on 6 April 2021.

The following items were packaged with the samples:

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

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

### 2.8 Instructions to Participants

Participants were instructed as follows:

- Quantitatively analyse the samples using your routine test method.
- Participants need not test for all listed analytes.

- For each analyte in each sample report a single result on as received basis in units of mg/kg.
- Report results as you would report 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 (e.g. $0.50 \pm 0.02$ mg/kg).
- Report any listed pesticide not tested with NT as the result.
- 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 the basis of your uncertainty estimates as requested in the results sheet (e.g. uncertainty budget, repeatability precision, long term result variability).
- If determined, report your percentage recovery. This will be presented in the report for information only.
- Please complete the method details as requested in the Methodology sheet.
- Please return the completed results sheet by email (proficiency@measurement.gov.au).
- Return the completed results sheet by 3 May 2021. Late results may not be included in the study report.

The results due date was extended to 17 May 2021 due to sample delivery delays to some participants.

### 2.9 Interim Report

An interim report was emailed to all participants on 20 May 2021.

## 3 PARTICIPANT LABORATORY INFORMATION

### 3.1 Test Methods Reported by Participants

Participants were requested to provide information about their test methods. Responses received are presented in Appendix 3.

### 3.2 Basis of Participants' Measurement Uncertainty Estimates

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

Table 3 Basis of Uncertainty Estimate

| Lab. Code | Approach to Estimating MU | Information Sources for MU Estimation* | | Guide Document for Estimating MU |
|---|---|---|---|---|
| | | Precision | Method Bias | |
| 1 | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS<br>Duplicate analysis | Laboratory bias from PT studies<br>Recoveries of SS<br>Standard purity | Eurachem/CITAC Guide |
| 3 | Standard deviation of replicate analyses multiplied by 2 or 3 | Duplicate analysis | Recoveries of SS | |
| 4 | Bottom Up (ISO/GUM, fish bone/cause and effect diagram) | Control samples<br>Duplicate analysis<br>Instrument calibration | Instrument calibration<br>Recoveries of SS | Eurachem/CITAC Guide |
| 5 | Bottom Up (ISO/GUM, fish bone/cause and effect diagram) | Control samples<br>Duplicate analysis<br>Instrument calibration | Recoveries of SS | ISO/GUM |
| 7 | Standard deviation of replicate analyses multiplied by 2 or 3 | Control samples - SS | | Nata Technical Note 33 |
| 8 | Top Down - precision and estimates of the method and laboratory bias | Control samples - RM<br>Duplicate analysis | CRM<br>Instrument calibration | NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results |
| 9 | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS | CRM<br>Recoveries of SS | ISO/GUM |
| 10 | Top Down - precision and estimates of the method and laboratory bias | Duplicate analysis | Recoveries of SS | |
| 11 | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS | | NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results |
| 12 | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS<br>Duplicate analysis | Recoveries of SS | Eurachem/CITAC Guide |
| 13 | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS<br>Duplicate analysis<br>Instrument calibration | | NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results |

| Lab. Code | Approach to Estimating MU | Information Sources for MU Estimation* | | Guide Document for Estimating MU |
|---|---|---|---|---|
| | | Precision | Method Bias | |
| 14 | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS<br>Duplicate analysis | CRM<br>Laboratory bias from PT studies<br>Recoveries of SS<br>Standard purity | NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results |
| 15 | Bottom Up (ISO/GUM, fish bone/cause and effect diagram) | Duplicate analysis | Instrument calibration<br>Recoveries of SS<br>Standard purity | ISO/GUM |
| 16 | Bottom Up (ISO/GUM, fish bone/cause and effect diagram) | Control samples<br>Instrument calibration | Instrument calibration<br>Recoveries of SS<br>Standard purity | ISO/GUM |
| 17 | Bottom Up (ISO/GUM, fish bone/cause and effect diagram) | Duplicate analysis | Recoveries of SS | Eurachem/CITAC Guide |
| 18 | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS | Recoveries of SS | NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results |
| 19 | Top Down - precision and estimates of the method and laboratory bias | Duplicate analysis<br>Instrument calibration | CRM<br>Instrument calibration<br>Recoveries of SS | NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results |
| 20 | Bottom Up (ISO/GUM, fish bone/cause and effect diagram) | Control samples - SS<br>Duplicate analysis | | |
| 21 | Top Down - precision and estimates of the method and laboratory bias | Control samples | CRM | NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results |
| 22 | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS | Recoveries of SS<br>Standard purity | NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results |
| 23 | Top Down - precision and estimates of the method and laboratory bias | Instrument calibration | Recoveries of SS | NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results |
| 24 | Standard uncertainty based on historical data | Duplicate analysis<br>Instrument calibration | CRM<br>Instrument calibration<br>Standard purity | Eurachem/CITAC Guide |

* CRM = Certified Reference Material; RM = Reference Material; SS = Spiked Samples

### 3.3 Participants' Comments

Participants were invited to make comments on the samples, study, or possible future studies. Such feedback may be useful in improving future studies. Participants' comments are presented in Table 4. Some comments may be modified so that the participant cannot be identified.

Table 4 Participants' Comments

| Lab. Code | Sample | Participant's Comments |
|---|---|---|
| 5 | S1 | Standard Addition was used |
| | S2 | Standard Addition was used |
| 8 | S1 | ND = screen extraction for but not detected (<0.01 ug/L in extraction solution) |
| | S2 | ND = screen extraction for but not detected (<0.01 ug/L in extraction solution) |
| 20 | S2 | spike recovery results: 2,4-D (82.4 %), Atrazine (95.6%), Glyphosate (117%), MCPA (122%), Simazine (78%), Triclopyr (101%), Lindane (96.7%), Heptachlor (112.6%), Aldrin (106.3%), Dieldrin (96.1%), Endrin (104.7%), DDT (81%) |

# 4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

## 4.1 Results Summary

Participant results are listed in Tables 5 to 11 with the summary statistics: robust average, median, mean, numeric results (N), maximum (Max.), minimum (Min.), robust standard deviation (robust SD) and robust coefficient of variation (robust CV). Bar charts of results and performance scores are presented in Figures 2 to 8, with an example chart with interpretation guide shown in Figure 1.

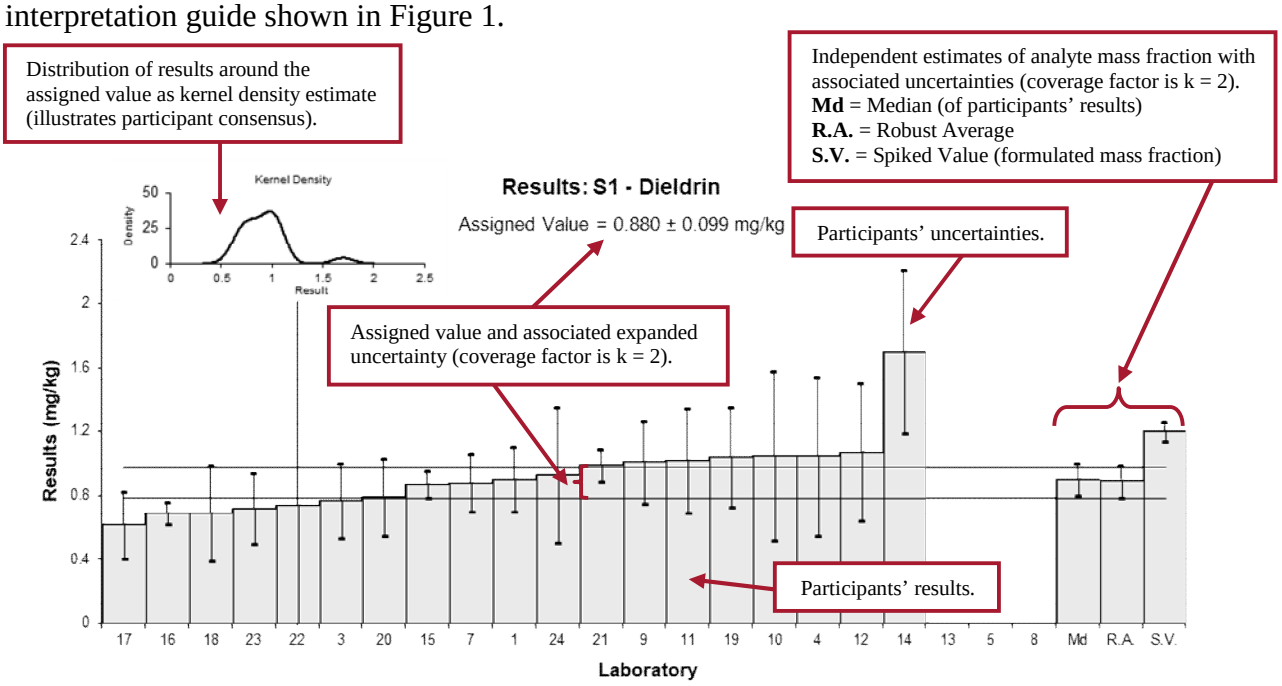



Figure 1 Guide to Presentation of Results

## 4.2 Outliers and Extreme Outliers

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.[3,4] Extreme outliers, if applicable, were obvious blunders, e.g. results with incorrect units, or for a different analyte or sample (gross errors), and such results were removed for the calculation of all summary statistics.[3]

## 4.3 Assigned Value

The assigned value is defined as the: 'value attributed to a particular property of a proficiency test item'.[1] In this PT study, the property is the mass fraction of the analytes in the samples. Assigned values were the robust averages of participants' results and the expanded uncertainties were estimated from the associated robust SDs (Appendix 4).

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

The robust averages and associated expanded MUs, and robust CVs (a measure of the variability of participants' results) were calculated as described in ISO 13528:2015.[7]

## 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 levels of analytes present. The PCV is not the CV of participants' results; it is set by the study coordinator and is based on the mass fraction of the analytes and experience from previous studies, and is supported by mathematical models such as the Thompson-Horwitz equation.[8] By setting a fixed and realistic value for the PCV, a participant's performance does not depend on other participants' performance and can be compared from study to study.

### 4.6 Target Standard Deviation

The target standard deviation (σ) is the product of the assigned value ($X$) and the PCV, as presented in Equation 1. This value is used for calculation of z-scores.

$$\sigma = X \times PCV \qquad \textit{Equation 1}$$

### 4.7 z-Score

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

$$z = \frac{(\chi - X)}{\sigma} \qquad \textit{Equation 2}$$

where:

$z$ is z-score

$\chi$ is a participant's result

$X$ is the assigned value

$\sigma$ is the target standard deviation from Equation 1

For the absolute value of a z-score:

- $|z| \leq 2.0$ is satisfactory;
- $2.0 < |z| < 3.0$ is questionable;
- $|z| \geq 3.0$ is unsatisfactory.

### 4.8 $E_n$-Score

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

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

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:

- $|E_n| \leq 1.0$ is satisfactory;
- $|E_n| > 1.0$ is unsatisfactory.

### 4.9 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC 17025 must establish and demonstrate the traceability and measurement uncertainty associated with their test results.[9]

Guidelines for quantifying uncertainty in analytical measurement are described in the Eurachem/CITAC Guide.[10]

## 5 TABLES AND FIGURES

Table 5

**Sample Details**

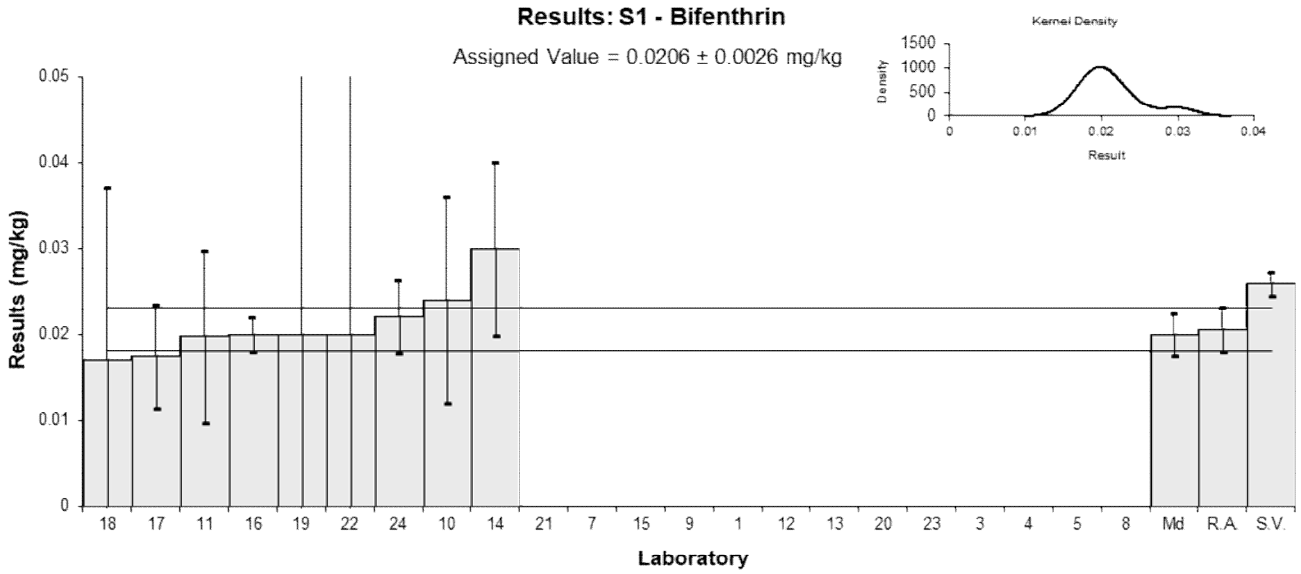
| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Soil |
| **Analyte** | Bifenthrin |
| **Units** | mg/kg |

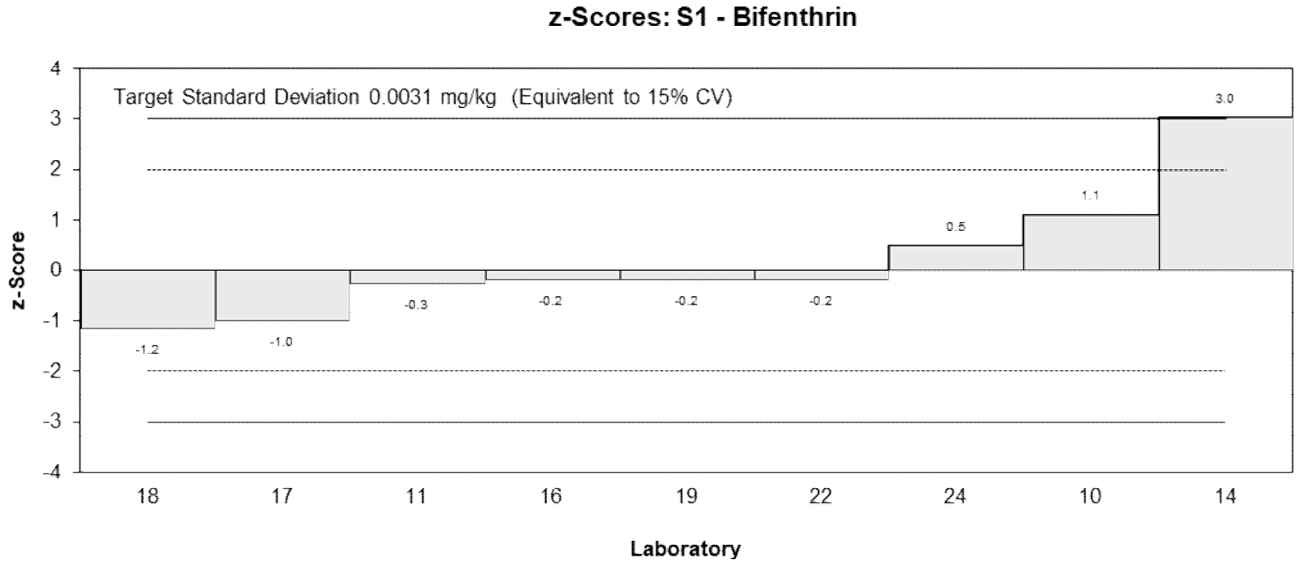
**Participant Results**

| Lab. Code | Result | Uncertainty | Recovery | z-Score | $E_n$-Score |
|---|---|---|---|---|---|
| **1** | NT | NT | NT | | |
| **3** | NT | NT | NT | | |
| **4** | NT | NT | NT | | |
| **5** | NT | NT | NT | | |
| **7** | <0.05 | 0.013 | NR | | |
| **8** | NT | NT | NT | | |
| **9** | NR | NR | NR | | |
| **10** | 0.024 | 0.012 | 116 | 1.10 | 0.28 |
| **11** | 0.0198 | 0.010 | NR | -0.26 | -0.08 |
| **12** | NT | NT | NT | | |
| **13** | NT | NT | NT | | |
| **14** | 0.030 | 0.010 | 70 | 3.04 | 0.91 |
| **15** | <0.2 | NR | NR | | |
| **16** | 0.02 | 0.002 | 84 | -0.19 | -0.18 |
| **17** | 0.0175 | 0.0060 | 75 | -1.00 | -0.47 |
| **18** | 0.017 | 0.02 | 49 | -1.17 | -0.18 |
| **19** | 0.02 | 0.07 | NR | -0.19 | -0.01 |
| **20** | NT | NT | NT | | |
| **21** | < 0.05 | 0.02 | NR | | |
| **22** | 0.02 | 32 | 103 | -0.19 | 0.00 |
| **23** | NT | NT | NT | | |
| **24** | 0.0221 | 0.0042 | NR | 0.49 | 0.30 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.0206 | 0.0026 |
| **Spike** | 0.0259 | 0.0013 |
| **Robust Average** | 0.0206 | 0.0026 |
| **Median** | 0.0200 | 0.0024 |
| **Mean** | 0.0212 | |
| **N** | 9 | |
| **Max.** | 0.030 | |
| **Min.** | 0.017 | |
| **Robust SD** | 0.0031 | |
| **Robust CV** | 15% | |


Results: S1 - Bifenthrin
Assigned Value = 0.0206 ± 0.0026 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
18 17 11 16 19 22 24 10 14 21 7 15 9 1 12 13 20 23 3 4 5 8 Md R.A. S.V.


z-Scores: S1 - Bifenthrin
Target Standard Deviation 0.0031 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
18 17 11 16 19 22 24 10 14
-1.2 -1.0 -0.3 -0.2 -0.2 -0.2 0.5 1.1 3.0

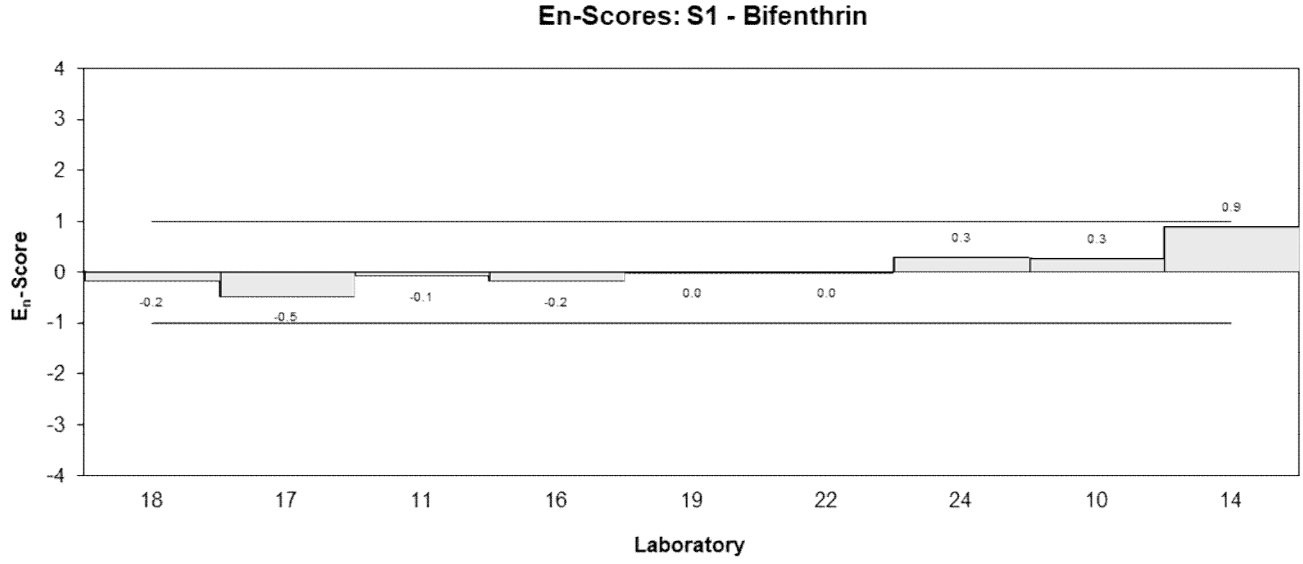

En-Scores: S1 - Bifenthrin
En-Score
Laboratory
18 17 11 16 19 22 24 10 14
-0.2 -0.5 -0.1 -0.2 0.0 0.0 0.3 0.3 0.9

Figure 2

Table 6

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Soil |
| **Analyte** | Cyfluthrin |
| **Units** | mg/kg |

**Participant Results**

| Lab. Code | Result | Uncertainty | Recovery |
|---|---|---|---|
| **1** | 0.02 | 0.006 | NR |
| **3** | <0.05 | NR | NR |
| **4** | NT | NT | NT |
| **5** | NT | NT | NT |
| **7** | NT | NT | NT |
| **8** | NT | NT | NT |
| **9** | NT | NT | NT |
| **10** | <0.05 | NR | NR |
| **11** | NT | NT | NT |
| **12** | NT | NT | NT |
| **13** | NT | NT | NT |
| **14** | NR | NR | NR |
| **15** | <0.4 | NR | NR |
| **16** | 0.01 | 0.001 | 90 |
| **17** | 0.0133 | 0.0045 | 78 |
| **18** | NT | NT | NT |
| **19** | < 2.0 | 0.6 | NR |
| **20** | NT | NT | NT |
| **21** | NT | NT | NT |
| **22** | <0.05 | NR | NR |
| **23** | NT | NT | NT |
| **24** | 0.0153 | 0.0088 | NR |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | Not Set | |
| **Spike** | 0.0195 | 0.0010 |
| **Robust Average** | 0.0147 | 0.0059 |
| **Median** | 0.0143 | 0.0063 |
| **Mean** | 0.0147 | |
| **N** | 4 | |
| **Max.** | 0.02 | |
| **Min.** | 0.01 | |
| **Robust SD** | 0.0047 | |
| **Robust CV** | 32% | |

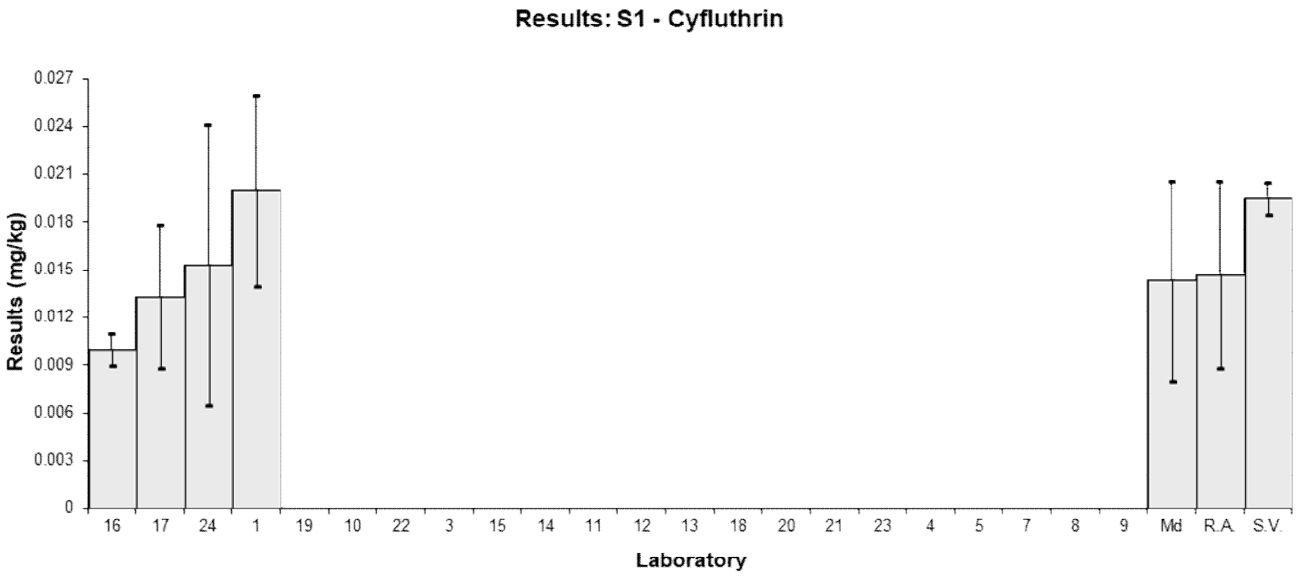

Results: S1 - Cyfluthrin
Results (mg/kg)
0.027
0.024
0.021
0.018
0.015
0.012
0.009
0.006
0.003
0
16
17
24
1
19
10
22
3
15
14
11
12
13
18
20
21
23
4
5
7
8
9
Md
R.A.
S.V.
Laboratory

Figure 3

Table 7

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Soil |
| **Analyte** | Dieldrin |
| **Units** | mg/kg |

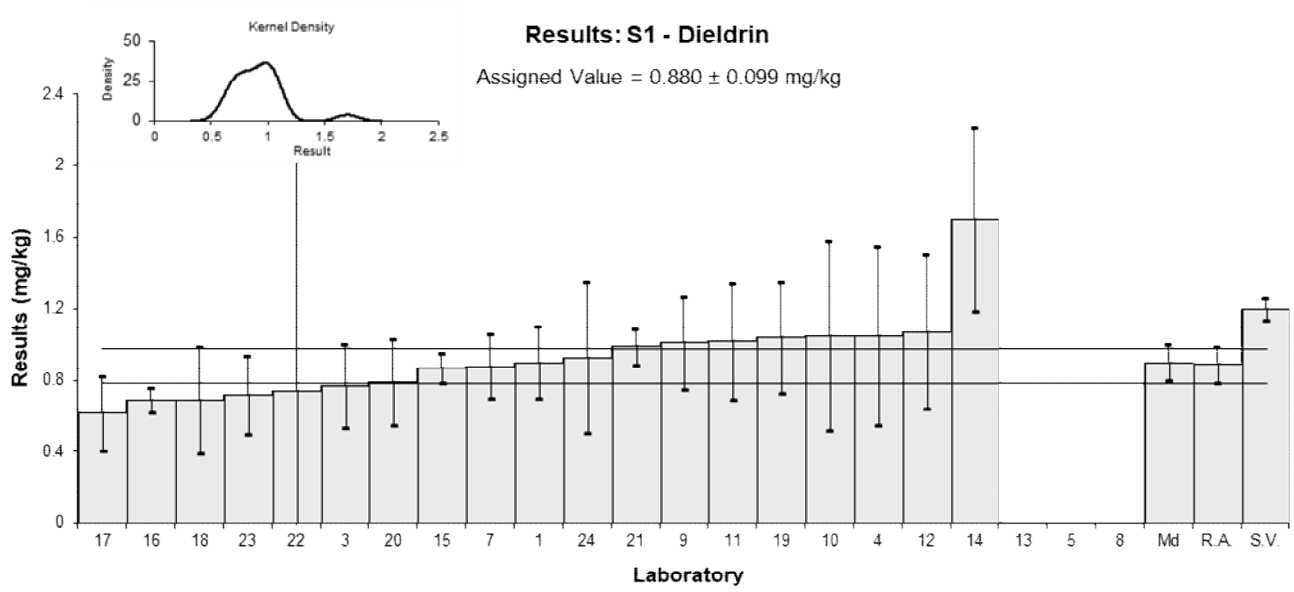
**Participant Results**

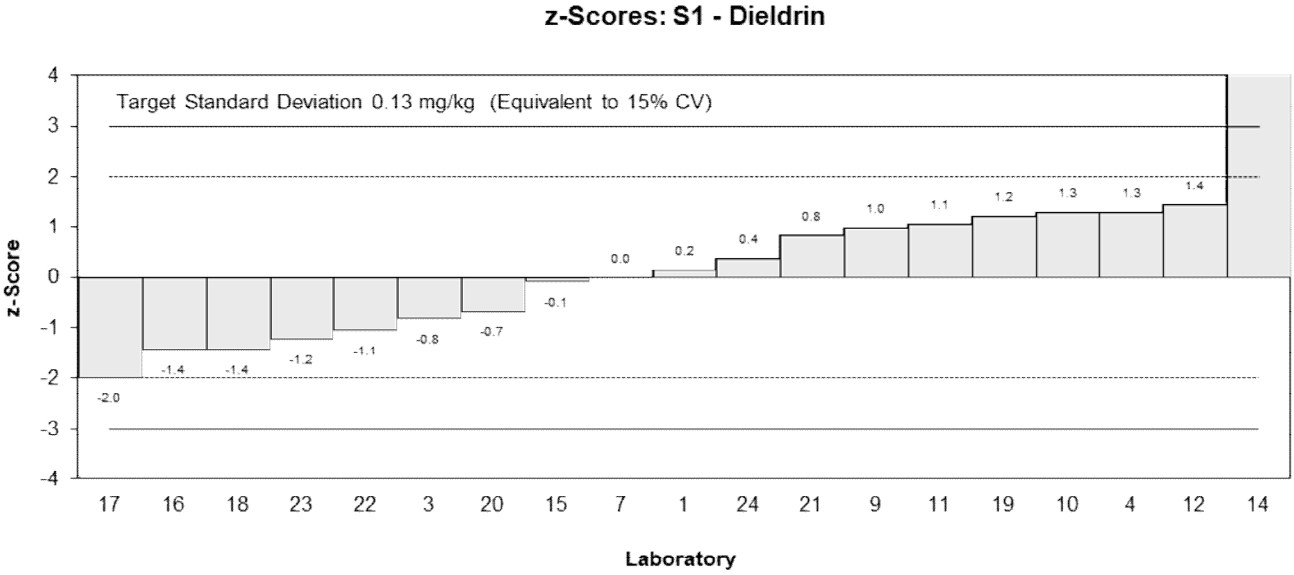
| Lab. Code | Result | Uncertainty | Recovery | z-Score | $E_n$-Score |
|---|---|---|---|---|---|
| **1** | 0.9 | 0.2 | 80 | 0.15 | 0.09 |
| **3** | 0.77 | 0.231 | 82.9 | -0.83 | -0.44 |
| **4** | 1.05 | 0.50 | NR | 1.29 | 0.33 |
| **5** | NT | NT | NT | | |
| **7** | 0.88 | 0.18 | NR | 0.00 | 0.00 |
| **8** | NT | NT | NT | | |
| **9** | 1.01 | 0.26 | 89 | 0.98 | 0.47 |
| **10** | 1.05 | 0.53 | 65 | 1.29 | 0.32 |
| **11** | 1.02 | 0.326 | NR | 1.06 | 0.41 |
| **12** | 1.07 | 0.43 | 101 | 1.44 | 0.43 |
| **13** | NT | NT | NT | | |
| **14** | 1.7 | 0.51 | 90 | 6.21 | 1.58 |
| **15** | 0.87 | 0.08 | NR | -0.08 | -0.08 |
| **16** | 0.69 | 0.07 | 90 | -1.44 | -1.57 |
| **17** | 0.616 | 0.209 | 76 | -2.00 | -1.14 |
| **18** | 0.69 | 0.3 | 78 | -1.44 | -0.60 |
| **19** | 1.04 | 0.31 | NR | 1.21 | 0.49 |
| **20** | 0.79 | 0.24 | NR | -0.68 | -0.35 |
| **21** | 0.99 | 0.1 | NR | 0.83 | 0.78 |
| **22** | 0.74 | 33 | 97 | -1.06 | 0.00 |
| **23** | 0.719 | 0.216 | NR | -1.22 | -0.68 |
| **24** | 0.93 | 0.42 | NR | 0.38 | 0.12 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value*** | 0.880 | 0.099 |
| **Spike** | 1.20 | 0.06 |
| **Robust Average** | 0.89 | 0.10 |
| **Median** | 0.90 | 0.10 |
| **Mean** | 0.92 | |
| **N** | 19 | |
| **Max.** | 1.7 | |
| **Min.** | 0.616 | |
| **Robust SD** | 0.18 | |
| **Robust CV** | 20% | |

* Robust average excluding Laboratory 14.


Results: S1 - Dieldrin
Assigned Value = 0.880 ± 0.099 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
17 16 18 23 22 3 20 15 7 1 24 21 9 11 19 10 4 12 14 13 5 8 Md R.A. S.V.


z-Scores: S1 - Dieldrin
Target Standard Deviation 0.13 mg/kg (Equivalent to 15% CV)
z-Score
-2.0 -1.4 -1.4 -1.2 -1.1 -0.8 -0.7 -0.1 0.0 0.2 0.4 0.8 1.0 1.1 1.2 1.3 1.3 1.4
Laboratory
17 16 18 23 22 3 20 15 7 1 24 21 9 11 19 10 4 12 14

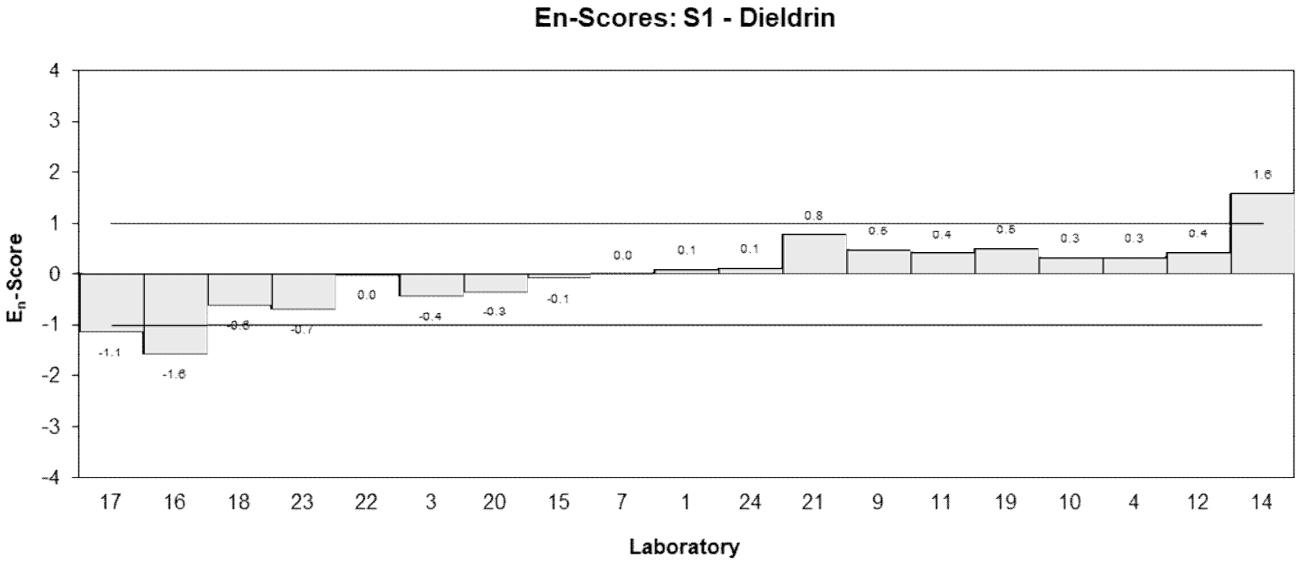

En-Scores: S1 - Dieldrin
En-Score
-1.1 -1.6 -0.6 -0.7 0.0 -0.4 -0.3 -0.1 0.0 0.1 0.1 0.8 0.5 0.4 0.5 0.3 0.3 0.4 1.6
Laboratory
17 16 18 23 22 3 20 15 7 1 24 21 9 11 19 10 4 12 14

Figure 4

Table 8

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Soil |
| **Analyte** | Glyphosate |
| **Units** | mg/kg |

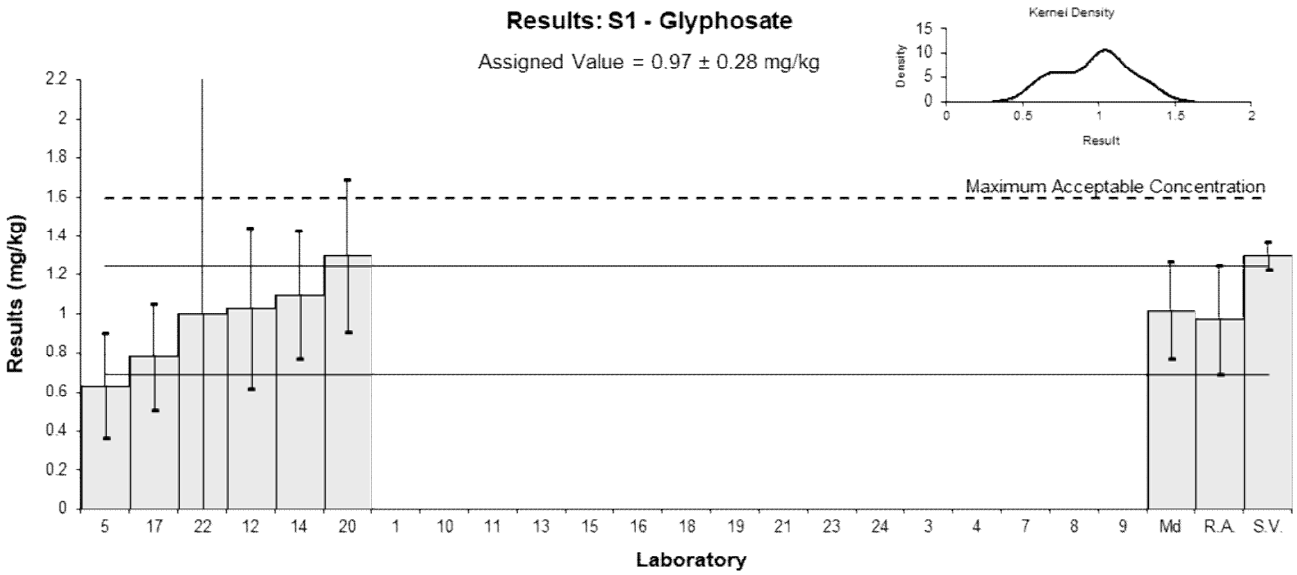
**Participant Results**

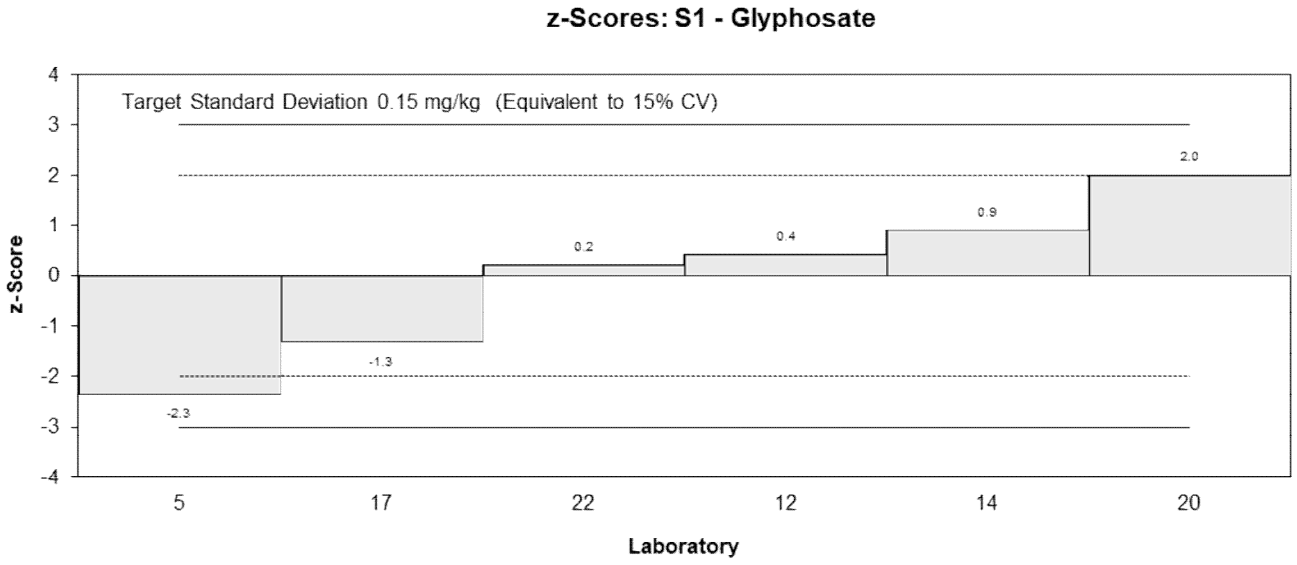
| Lab. Code | Result | Uncertainty | Recovery | z-Score | $E_n$-Score |
|---|---|---|---|---|---|
| **1** | <0.01 | NR | NR | | |
| **3** | NT | NT | NT | | |
| **4** | NT | NT | NT | | |
| **5** | 0.63 | 0.27 | NR | -2.34 | -0.87 |
| **7** | NT | NT | NT | | |
| **8** | NT | NT | NT | | |
| **9** | NT | NT | NT | | |
| **10** | NT | NT | NT | | |
| **11** | NT | NT | NT | | |
| **12** | 1.03 | 0.41 | 116 | 0.41 | 0.12 |
| **13** | NT | NT | NT | | |
| **14** | 1.1 | 0.33 | 90 | 0.89 | 0.30 |
| **15** | NT | NT | NT | | |
| **16** | NT | NT | NT | | |
| **17** | 0.779 | 0.273 | 76 | -1.31 | -0.49 |
| **18** | NT | NT | NT | | |
| **19** | NT | NT | NT | | |
| **20*** | 1.3 | 0.39 | NR | 2.00 | 0.69 |
| **21** | NT | NT | NT | | |
| **22** | 1.0 | 27 | 106 | 0.21 | 0.00 |
| **23** | NT | NT | NT | | |
| **24** | NT | NT | NT | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.97 | 0.28 |
| **Spike** | 1.30 | 0.07 |
| **Max. Acceptable Concentration*** | 1.59 | |
| **Robust Average** | 0.97 | 0.28 |
| **Median** | 1.02 | 0.25 |
| **Mean** | 0.97 | |
| **N** | 6 | |
| **Max.** | 1.3 | |
| **Min.** | 0.63 | |
| **Robust SD** | 0.27 | |
| **Robust CV** | 28% | |

* z-Score adjusted to 2.00 (see Section 6.3).


Results: S1 - Glyphosate
Assigned Value = 0.97 ± 0.28 mg/kg
Kernel Density
Density
Result
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
5 17 22 12 14 20 1 10 11 13 15 16 18 19 21 23 24 3 4 7 8 9 Md R.A. S.V.


z-Scores: S1 - Glyphosate
Target Standard Deviation 0.15 mg/kg (Equivalent to 15% CV)
z-Score
-2.3
-1.3
0.2
0.4
0.9
2.0
Laboratory
5 17 22 12 14 20

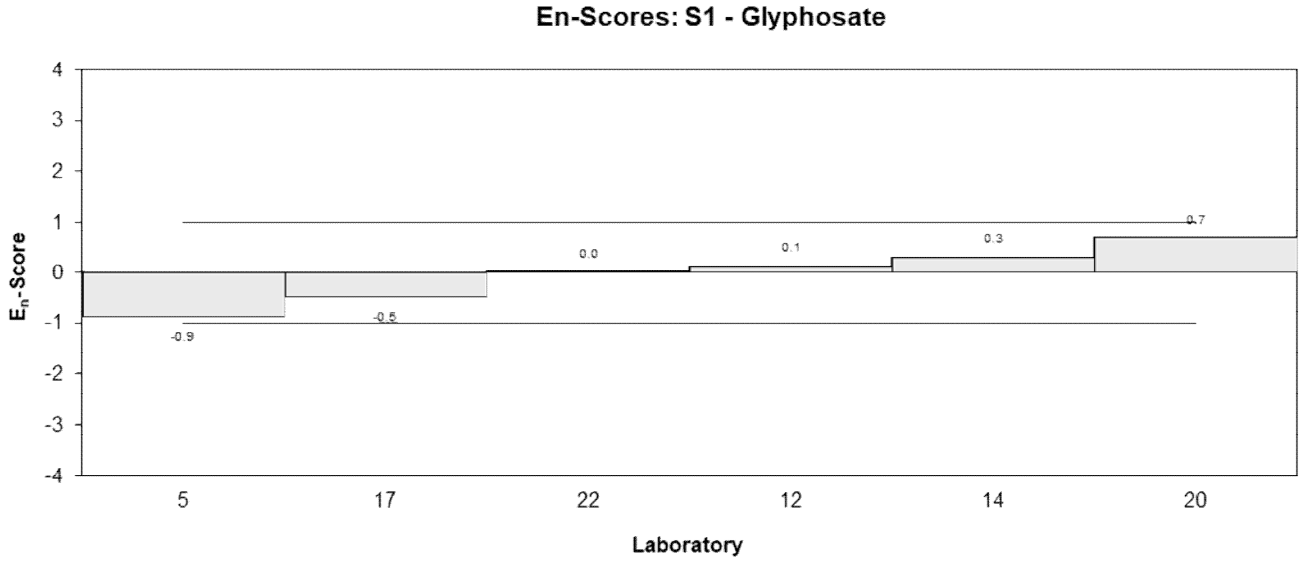

En-Scores: S1 - Glyphosate
En-Score
-0.9
-0.5
0.0
0.1
0.3
0.7
Laboratory
5 17 22 12 14 20

Figure 5

Table 9

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Soil |
| **Analyte** | Imidacloprid |
| **Units** | mg/kg |

**Participant Results**

| Lab. Code | Result | Uncertainty | Recovery |
|---|---|---|---|
| **1** | 0.08 | 0.02 | NR |
| **3** | 0.11 | 0.033 | 89 |
| **4** | NT | NT | NT |
| **5** | NT | NT | NT |
| **7** | NT | NT | NT |
| **8** | 0.1697 | 0.042 | 106 |
| **9** | NT | NT | NT |
| **10** | <0.05 | NR | NR |
| **11** | NT | NT | NT |
| **12** | NT | NT | NT |
| **13** | 0.83 | 0.249 | NR |
| **14** | 0.15 | 0.050 | 80 |
| **15** | NT | NT | NT |
| **16** | NT | NT | NT |
| **17** | NT | NT | NT |
| **18** | 0.17 | 0.043 | 93 |
| **19** | NT | NT | NT |
| **20** | NT | NT | NT |
| **21** | NT | NT | NT |
| **22** | 0.08 | 21 | 91 |
| **23** | NT | NT | NT |
| **24** | NT | NT | NT |

**Statistics***

| | | |
|---|---|---|
| **Assigned Value** | Not Set | |
| **Spike** | 0.151 | 0.008 |
| **Robust Average** | 0.127 | 0.049 |
| **Median** | 0.130 | 0.062 |
| **Mean** | 0.127 | |
| **N** | 6 | |
| **Max.** | 0.17 | |
| **Min.** | 0.08 | |
| **Robust SD** | 0.048 | |
| **Robust CV** | 38% | |

* After the release of the interim report, Laboratory 13 reported that their submitted result was incorrect, and so this result has been excluded from all statistical calculations.

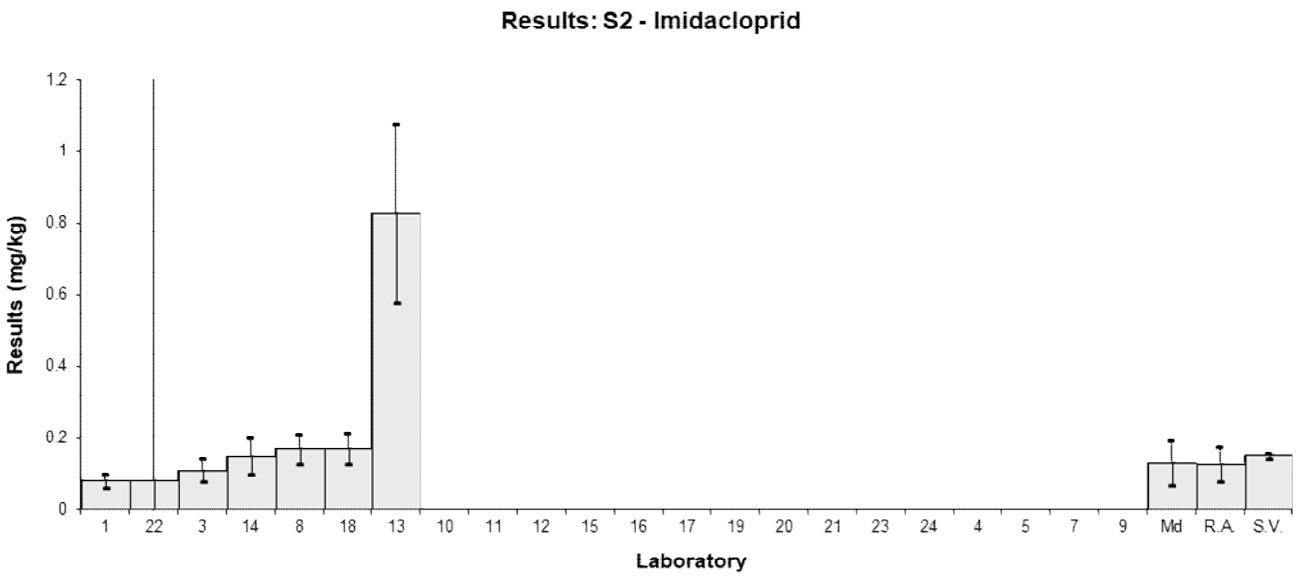

Results: S2 - Imidacloprid
Results (mg/kg)
1.2
1
0.8
0.6
0.4
0.2
0
1
22
3
14
8
18
13
10
11
12
15
16
17
19
20
21
23
24
4
5
7
9
Md
R.A.
S.V.
Laboratory

Figure 6

Table 10

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Soil |
| **Analyte** | p,p'-DDE |
| **Units** | mg/kg |

**Participant Results**

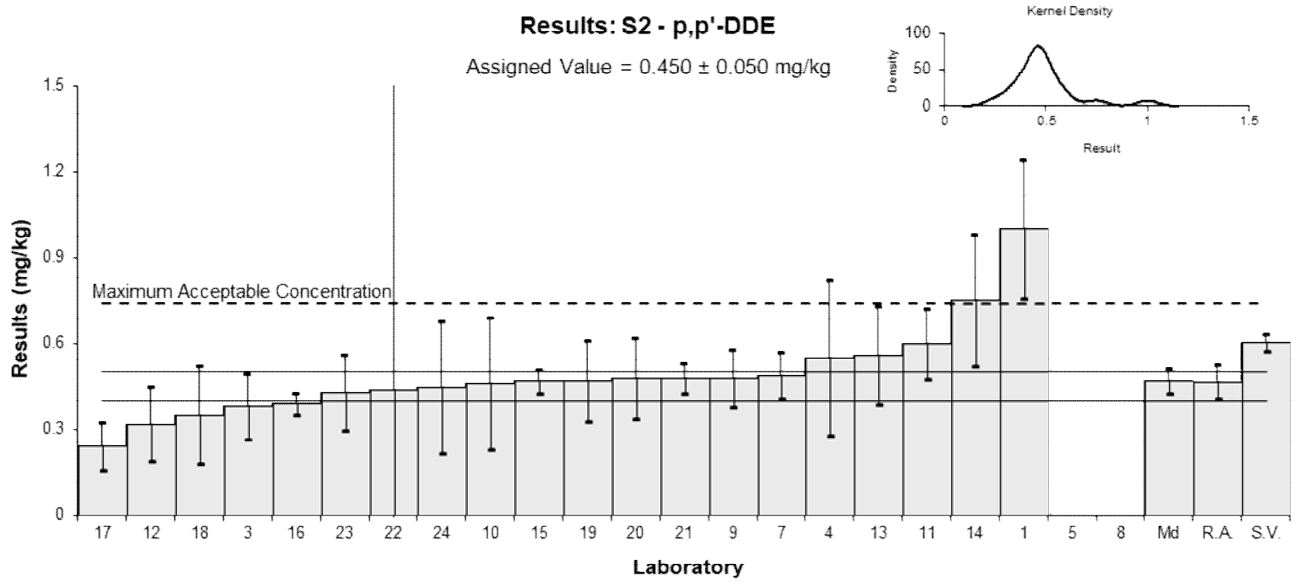
| Lab. Code | Result | Uncertainty | Recovery | z-Score | $E_n$-Score |
|---|---|---|---|---|---|
| **1** | 1 | 0.24 | 81 | 8.15 | 2.24 |
| **3** | 0.38 | 0.114 | 89.2 | -1.04 | -0.56 |
| **4** | 0.55 | 0.27 | NR | 1.48 | 0.36 |
| **5** | NT | NT | NT | | |
| **7** | 0.49 | 0.08 | NR | 0.59 | 0.42 |
| **8** | NT | NT | NT | | |
| **9** | 0.48 | 0.1 | 93 | 0.44 | 0.27 |
| **10** | 0.46 | 0.23 | 95 | 0.15 | 0.04 |
| **11**** | 0.602 | 0.123 | NR | 2.00 | 1.00 |
| **12** | 0.32 | 0.13 | NR | -1.93 | -0.93 |
| **13** | 0.56 | 0.17 | NR | 1.63 | 0.62 |
| **14** | 0.75 | 0.23 | 80 | 4.44 | 1.27 |
| **15** | 0.47 | 0.04 | NR | 0.30 | 0.31 |
| **16** | 0.39 | 0.04 | 92 | -0.89 | -0.94 |
| **17** | 0.244 | 0.083 | NR | -3.05 | -2.13 |
| **18** | 0.35 | 0.17 | 72 | -1.48 | -0.56 |
| **19** | 0.47 | 0.14 | NR | 0.30 | 0.13 |
| **20** | 0.48 | 0.14 | NR | 0.44 | 0.20 |
| **21** | 0.48 | 0.05 | NR | 0.44 | 0.42 |
| **22** | 0.44 | 26 | 101 | -0.15 | 0.00 |
| **23** | 0.43 | 0.13 | NR | -0.30 | -0.14 |
| **24** | 0.45 | 0.23 | NR | 0.00 | 0.00 |

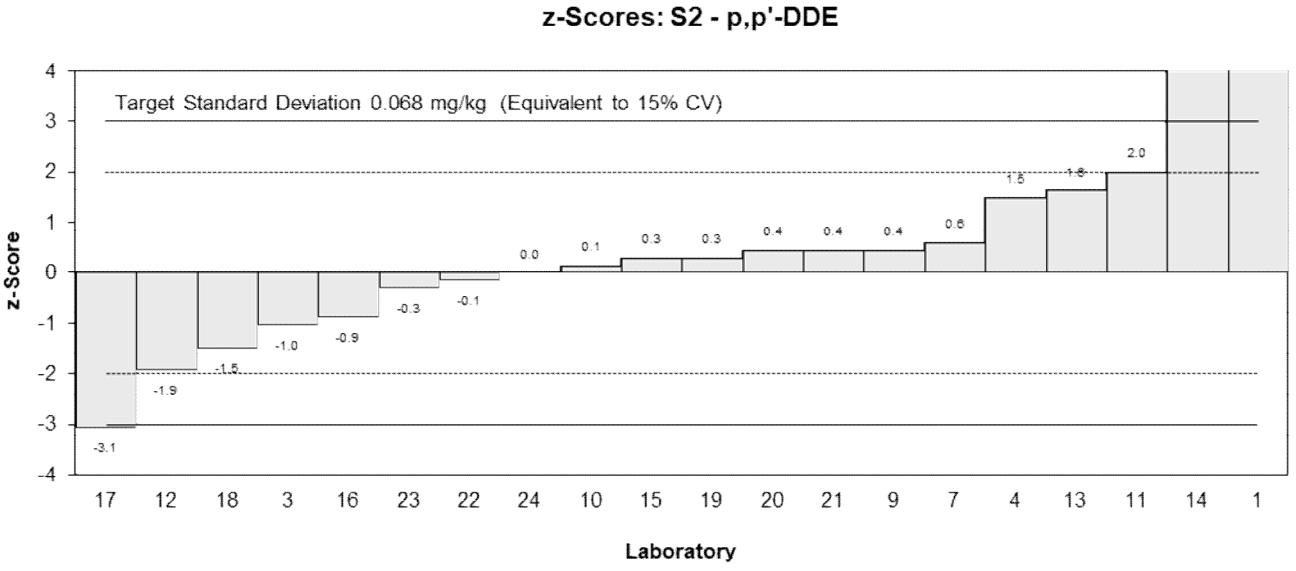
**Statistics**

| | | |
|---|---|---|
| **Assigned Value*** | 0.450 | 0.050 |
| **Spike** | 0.604 | 0.030 |
| **Max. Acceptable Concentration**** | 0.739 | |
| **Robust Average** | 0.468 | 0.058 |
| **Median** | 0.470 | 0.042 |
| **Mean** | 0.490 | |
| **N** | 20 | |
| **Max.** | 1 | |
| **Min.** | 0.244 | |
| **Robust SD** | 0.10 | |
| **Robust CV** | 22% | |

* Robust average excluding Laboratories 1 and 14.

** z-Score adjusted to 2.00 (see Section 6.3).


Results: S2 - p,p'-DDE
Assigned Value = 0.450 ± 0.050 mg/kg
Kernel Density
Density
Result
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
17 12 18 3 16 23 22 24 10 15 19 20 21 9 7 4 13 11 14 1 5 8 Md R.A. S.V.


z-Scores: S2 - p,p'-DDE
Target Standard Deviation 0.068 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
17 12 18 3 16 23 22 24 10 15 19 20 21 9 7 4 13 11 14 1

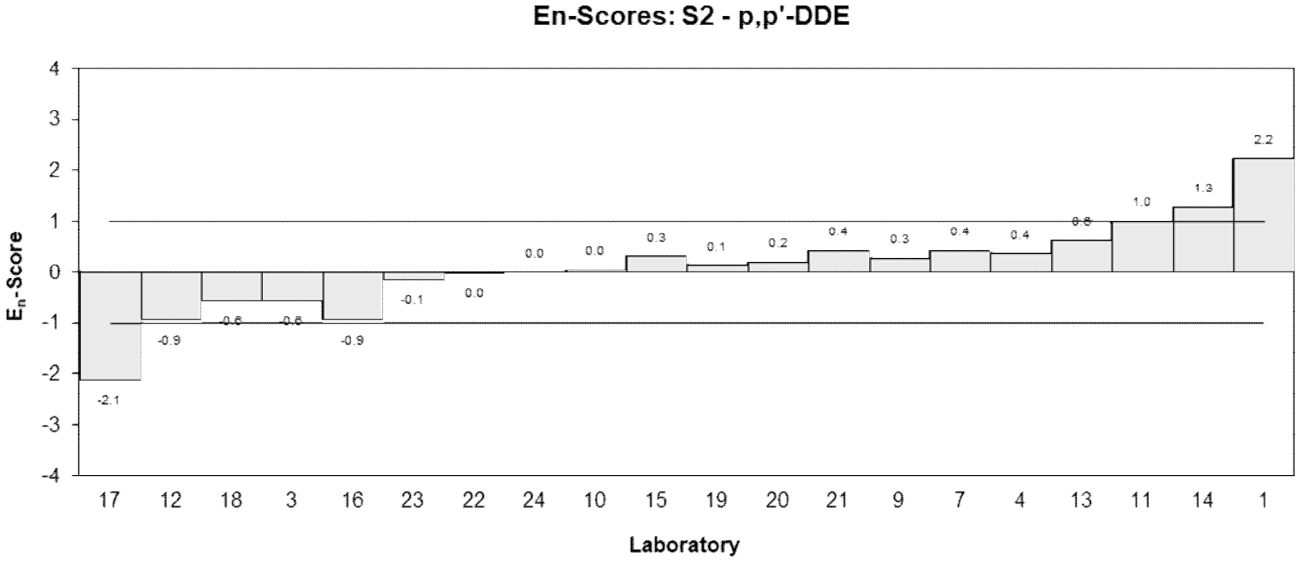

En-Scores: S2 - p,p'-DDE
En-Score
Laboratory
17 12 18 3 16 23 22 24 10 15 19 20 21 9 7 4 13 11 14 1

Figure 7

Table 11

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Soil |
| **Analyte** | *trans*-Chlordane |
| **Units** | mg/kg |

**Participant Results**

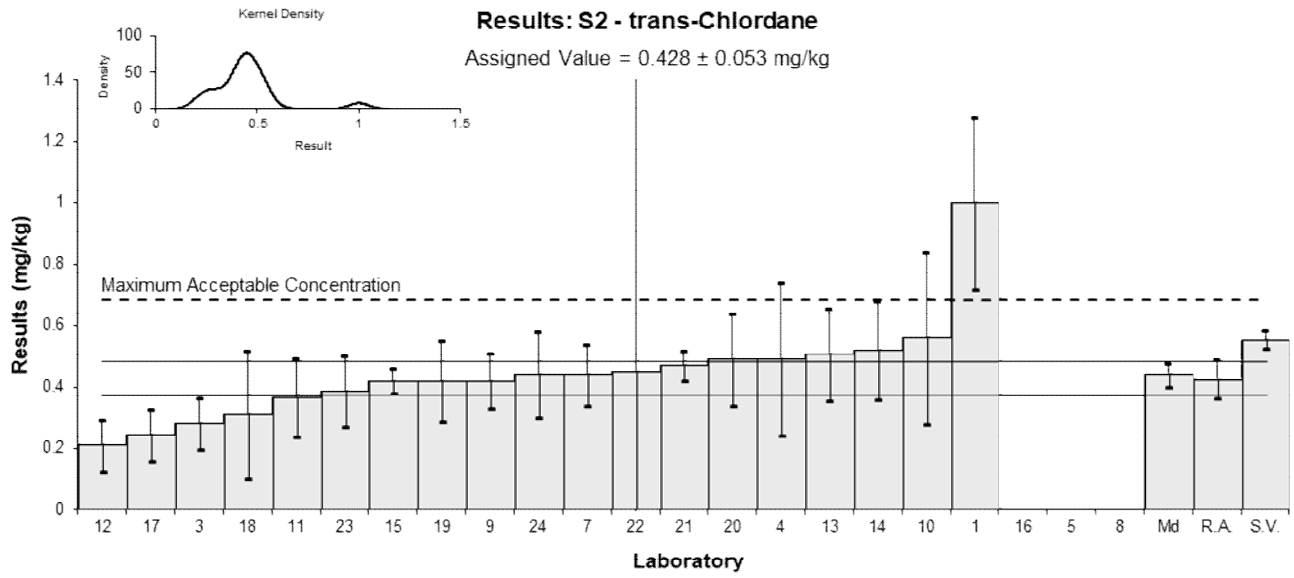
| Lab. Code | Result | Uncertainty | Recovery | z-Score | $E_n$-Score |
|---|---|---|---|---|---|
| **1** | 1 | 0.28 | 93 | 8.91 | 2.01 |
| **3** | 0.28 | 0.084 | 70.7 | -2.31 | -1.49 |
| **4** | 0.49 | 0.25 | NR | 0.97 | 0.24 |
| **5** | NT | NT | NT | | |
| **7** | 0.44 | 0.1 | NR | 0.19 | 0.11 |
| **8** | NT | NT | NT | | |
| **9** | 0.42 | 0.09 | 89 | -0.12 | -0.08 |
| **10**** | 0.56 | 0.28 | 122 | 2.00 | 0.46 |
| **11** | 0.365 | 0.127 | NR | -0.98 | -0.46 |
| **12** | 0.21 | 0.084 | NR | -3.40 | -2.19 |
| **13** | 0.506 | 0.15 | NR | 1.21 | 0.49 |
| **14** | 0.52 | 0.16 | 90 | 1.43 | 0.55 |
| **15** | 0.42 | 0.04 | NR | -0.12 | -0.12 |
| **16** | NT | NT | NT | | |
| **17** | 0.243 | 0.083 | NR | -2.88 | -1.88 |
| **18** | 0.31 | 0.21 | 67 | -1.84 | -0.54 |
| **19** | 0.42 | 0.13 | NR | -0.12 | -0.06 |
| **20** | 0.49 | 0.15 | NR | 0.97 | 0.39 |
| **21** | 0.47 | 0.05 | NR | 0.65 | 0.58 |
| **22** | 0.45 | 30 | 94 | 0.34 | 0.00 |
| **23** | 0.387 | 0.116 | NR | -0.64 | -0.32 |
| **24** | 0.44 | 0.14 | NR | 0.19 | 0.08 |

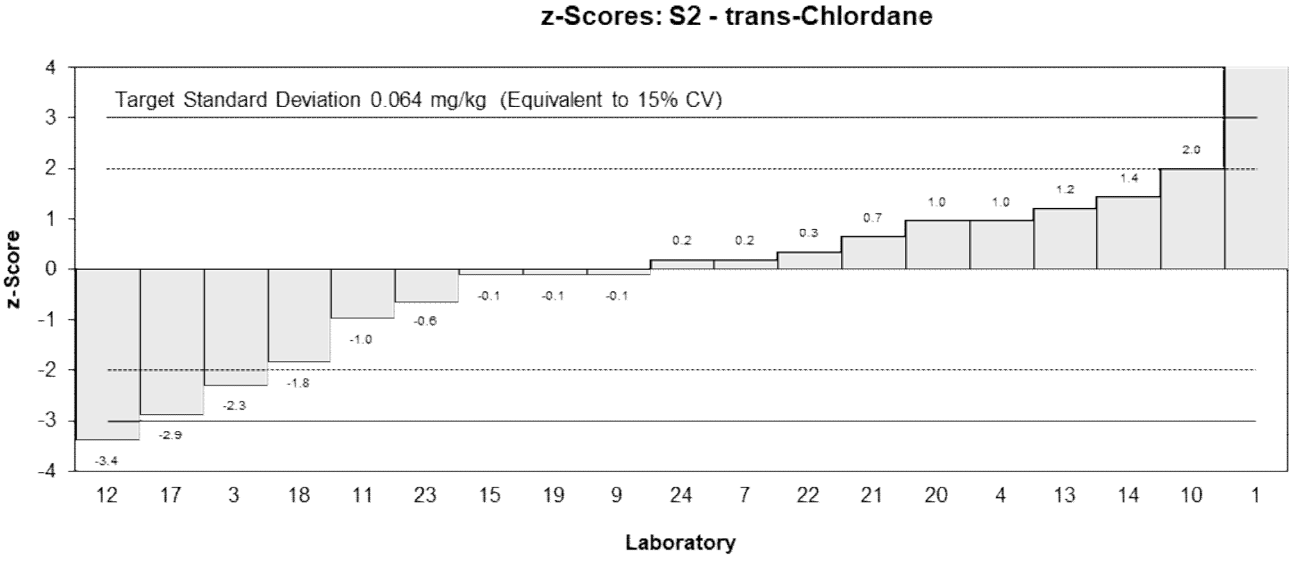
**Statistics**

| | | |
|---|---|---|
| **Assigned Value*** | 0.428 | 0.053 |
| **Spike** | 0.555 | 0.028 |
| **Max. Acceptable Concentration**** | 0.683 | |
| **Robust Average** | 0.425 | 0.062 |
| **Median** | 0.440 | 0.038 |
| **Mean** | 0.443 | |
| **N** | 19 | |
| **Max.** | 1 | |
| **Min.** | 0.21 | |
| **Robust SD** | 0.11 | |
| **Robust CV** | 25% | |

* Robust average excluding Laboratories 1 and 12.

** z-Score adjusted to 2.00 (see Section 6.3).


Kernel Density
Density
Result
Results: S2 - trans-Chlordane
Assigned Value = 0.428 ± 0.053 mg/kg
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
12 17 3 18 11 23 15 19 9 24 7 22 21 20 4 13 14 10 1 16 5 8 Md R.A. S.V.


z-Scores: S2 - trans-Chlordane
Target Standard Deviation 0.064 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
12 17 3 18 11 23 15 19 9 24 7 22 21 20 4 13 14 10 1

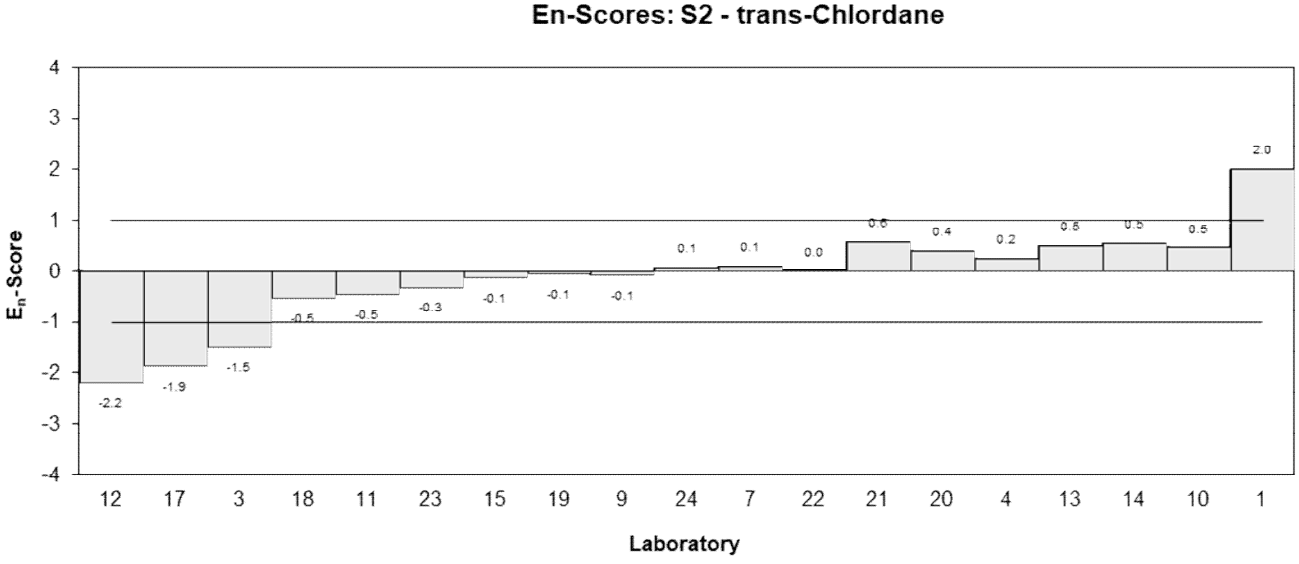

En-Scores: S2 - trans-Chlordane
En-Score
Laboratory
12 17 3 18 11 23 15 19 9 24 7 22 21 20 4 13 14 10 1

Figure 8

## 6 DISCUSSION OF RESULTS

### 6.1 Assigned Value

The robust averages of participants' results were used as the assigned values for all scored analytes. The robust averages and associated expanded uncertainties were calculated using the procedure described in ISO 13528:2015.[7] Results less than 50% and greater than 150% of the robust average were removed before calculation of the assigned value.[3,4] The calculation of the expanded uncertainty for robust averages is presented in Appendix 4, using bifenthrin in Sample S1 as an example.

**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.

No assigned values were set for cyfluthrin in Sample S1 and imidacloprid in sample S2 as few numeric results were reported for these analytes, and reported results were highly variable.

A comparison of the assigned values (or robust average if no assigned value was set) and the spiked values is presented in Table 12. The assigned values were within the range of 73% to 80% of the spiked values; similar ratios have been observed in previous Pesticides in Soil PT studies and this provides good support for the assigned values. The best estimate of the 'true' mass fraction of the pesticides in the soil is most likely the spiked value. However, a proportion of the spiked pesticide is strongly bound to the soil and so is not readily extracted and measured. What laboratories actually measure may best be described as 'extractable pesticide', and the result may be influenced by the efficiency of the extraction process used. Whilst this may be an underestimate of the total amount of pesticide, it is likely that strongly bound pesticide is of little environmental significance. For this study, the assigned value is therefore the best estimate of the amount of 'extractable pesticide'.

Table 12 Comparison of Assigned Value (Robust Average) and Spiked Value

| Sample | Analyte | Assigned Value *(Robust Average)* (mg/kg) | Spiked Value (mg/kg) | Assigned Value *(Robust Average)* / Spiked Value (%) |
|---|---|---|---|---|
| S1 | Bifenthrin | 0.0206 | 0.0259 | 80 |
| | Cyfluthrin | *(0.0147)* | 0.0195 | *(75)* |
| | Dieldrin | 0.880 | 1.20 | 73 |
| | Glyphosate | 0.97 | 1.30 | 75 |
| S2 | Imidacloprid | *(0.127)* | 0.151 | *(84)* |
| | p,p'-DDE | 0.450 | 0.604 | 75 |
| | *trans*-Chlordane | 0.428 | 0.555 | 77 |

### 6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded uncertainty associated with their results and the basis of this uncertainty estimate. It is a requirement of ISO/IEC 17025:2017 that laboratories have procedures to estimate the uncertainty of chemical measurements and to report this uncertainty in specific circumstances, including when the client's instruction so requires.[9]

All 84 numerical results submitted for analytes of interest in this study were reported with an associated expanded MU. Participants used a wide variety of procedures to estimate their uncertainties (Table 3).

The magnitude of the reported expanded uncertainties was within the range 8.5% to 160000% of the reported value. In general, an expanded uncertainty of less than 15% is likely to be unrealistically small for the routine measurement of a pesticide residue, while over 50% is likely to be too large. In this study, ten expanded uncertainties were less than 15% relative while fourteen were greater than 50% relative. Laboratory **22**'s uncertainties ranged from 2700% to 160000% of their results; this participant may have reported uncertainties as relative instead of absolute values.

Uncertainties associated with results returning a satisfactory z-score but an unsatisfactory $E_n$-score may have been underestimated.

Laboratories **7**, **19** and **21** attached estimates of the expanded MU for results reported as less than their limit of reporting. An estimate of uncertainty expressed as a value cannot be attached to a result expressed as a range.[10]

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 0.719 ± 0.216 mg/kg, it is better to report this as 0.72 ± 0.22 mg/kg.[10]

### 6.3 z-Score

Target SDs equivalent to 15% PCV were used to calculate z-scores. CVs predicted by the Thomspon-Horwitz equation,[8] target SDs (as PCV), and between-laboratory CVs obtained in this study for scored analytes are presented for comparison in Table 13.

Table 13 Comparison of Thompson-Horwitz CVs, Target SDs and Between-Laboratory CVs

| Sample | Analyte | Assigned value (mg/kg) | Thompson-Horwitz CV (%) | Target SD (as PCV) (%) | Between-Laboratory CV* (%) |
|---|---|---|---|---|---|
| S1 | Bifenthrin | 0.0206 | 22 | 15 | 15 |
| | Dieldrin | 0.880 | 16 | 15 | 19 |
| | Glyphosate | 0.97 | 16 | 15 | 28 |
| S2 | p,p'-DDE | 0.450 | 18 | 15 | 19 |
| | *trans*-Chlordane | 0.428 | 18 | 15 | 21 |

* Robust between-laboratory CV with outliers removed, if applicable.

To account for possible low bias in consensus values due to participants using inefficient analytical or extraction techniques, a total of three z-scores were adjusted across the following analytes: Sample S1 glyphosate, and Sample S2 p,p'-DDE and *trans*-chlordane. A maximum acceptable concentration was set to two target SDs more than the spiked value, and results lower than the maximum acceptable concentration but with a z-score greater than 2.0 had their z-score adjusted to 2.0. This ensured that participants reporting results close to the spiked value were not penalised. z-Scores for results higher than the maximum acceptable concentration and z-scores less than 2.0 were left unaltered.

Of 73 results for which z-scores were calculated, 63 (86%) returned a satisfactory z-score of $|z| \leq 2.0$, indicating a satisfactory performance.

Laboratories **14**, **17** and **22** reported results for all five analytes for which z-scores were calculated. Laboratory **22** returned satisfactory z-scores for all five scored analytes.

Satisfactory z-scores were achieved for all scored results reported by Laboratories **10** (4), **11** (4), **18** (4), **19** (4), **20** (4), **24** (4), **4** (3), **7** (3), **9** (3), **15** (3), **21** (3), **23** (3), **16** (3) and **13** (2).

The dispersal of participants' z-scores is presented graphically by laboratory in Figure 9 and by analyte in Figure 10.

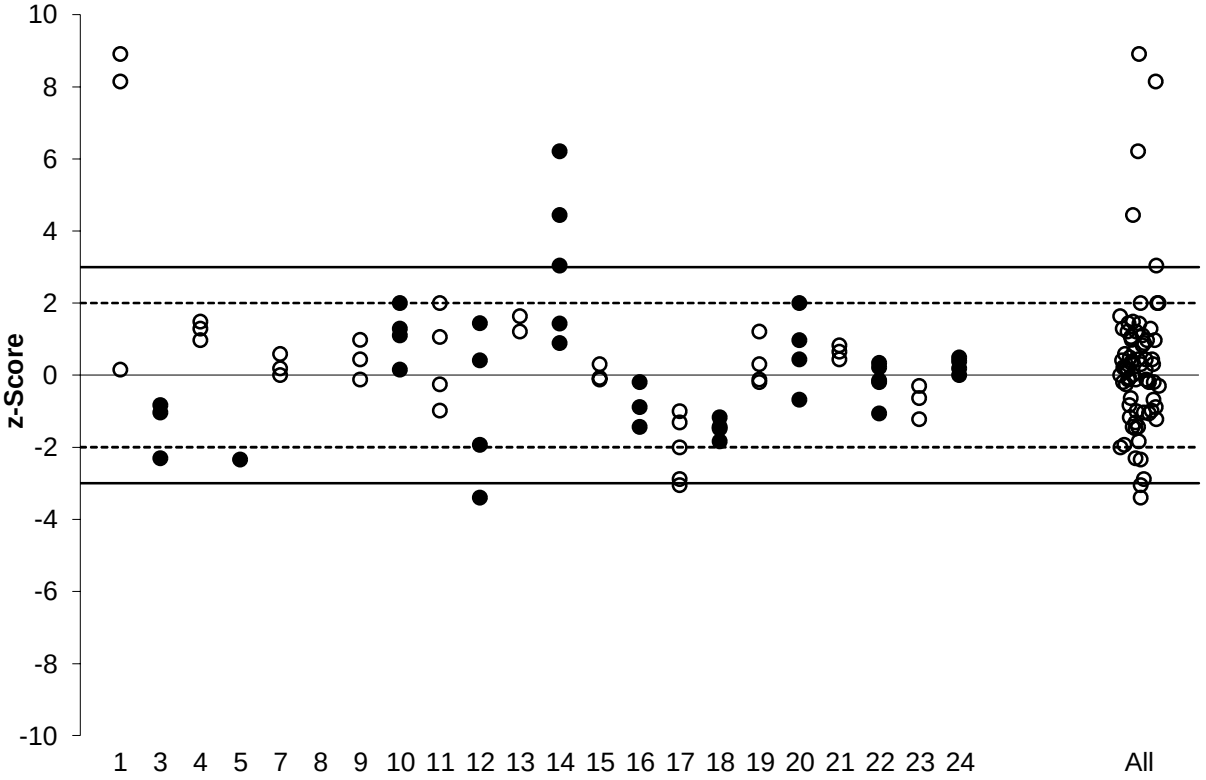



Figure 9 z-Score Dispersal by Laboratory

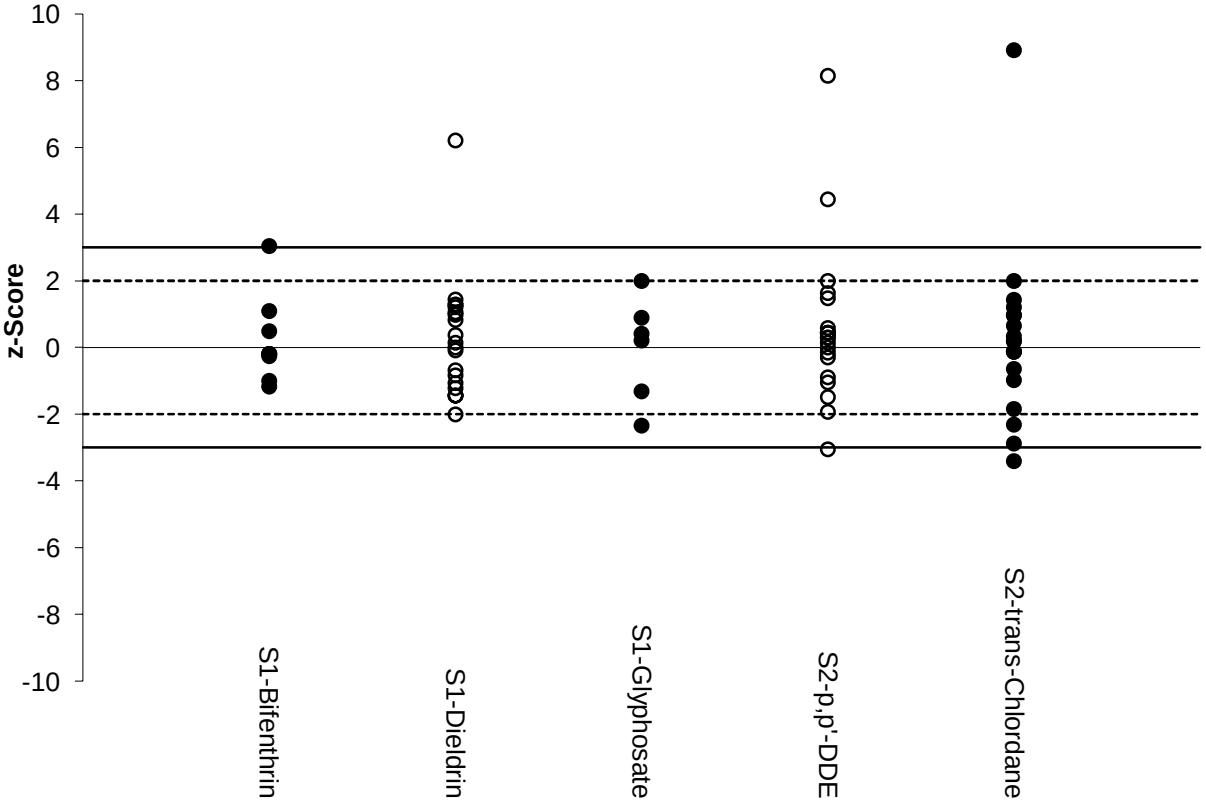



Figure 10 z-Score Dispersal by Analyte

### 6.4 $E_n$-Score

Where a laboratory did not report an expanded uncertainty with a result, an 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 z-Scores, $E_n$-scores greater than 1.0 were set to 1.0.

Of 73 results for which $E_n$-scores were calculated, 63 (86%) were satisfactory with $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective uncertainties.

Laboratory **22** returned $E_n$-scores with $|E_n| \leq 1.0$ for all scored analytes, though this participant reported unrealistically large uncertainties (ranging from 2700% to 160000% of their results).

Satisfactory $E_n$-scores were achieved for all scored results reported by Laboratories **10** (4), **11** (4), **18** (4), **19** (4), **20** (4), **24** (4), **4** (3), **7** (3), **9** (3), **15** (3), **21** (3), **23** (3), **13** (2) and **5** (1).

The dispersal of participants' $E_n$-scores is presented graphically by laboratory in Figure 11.

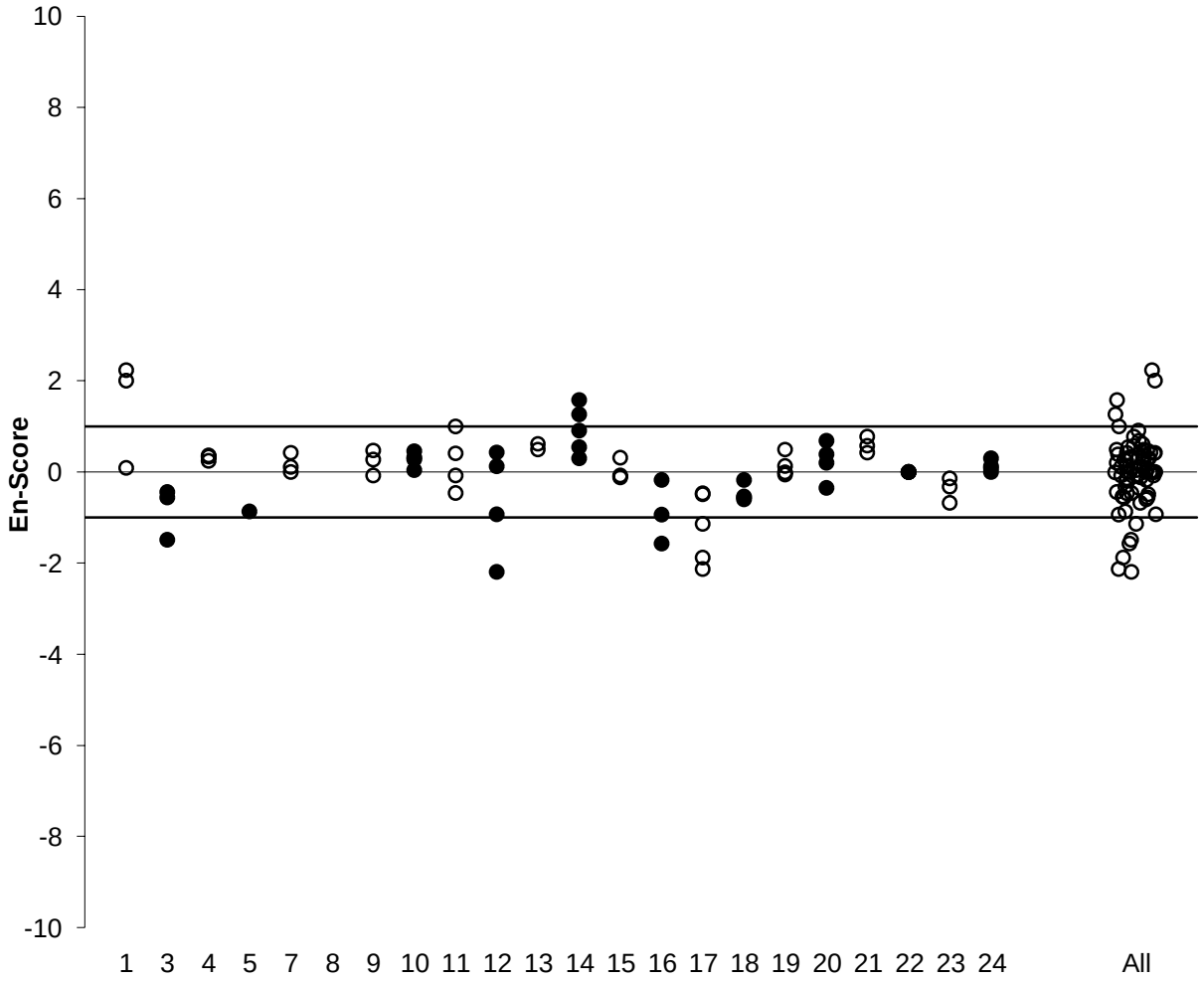



Figure 11 $E_n$-Score Dispersal by Laboratory

### 6.5 False Negatives

Table 14 presents false negative results – analytes present in the samples which a participant tested for but did not report a result (for example, participants reporting a 'less-than' result (<*x*) when the assigned and spiked values were higher than their limit of reporting (LOR), or laboratories that didn't report any value). For analytes where no assigned value was set, results have only been considered to be false negatives where the robust average and spiked value were significantly higher than the participants' LOR.

Table 14 False Negatives

| Lab. Code | Sample | Analyte | Assigned Value *(Robust Average)* (mg/kg) | Spiked Value (mg/kg) | Result (mg/kg) |
|---|---|---|---|---|---|
| 1 | S1 | Glyphosate | 0.97 | 1.30 | <0.01 |
| 9 | S1 | Bifenthrin | 0.0206 | 0.0259 | NR* |
| 10 | S2 | Imidacloprid | *(0.127)* | 0.151 | <0.05 |
| 14 | S1 | Cyfluthrin | *(0.0147)* | 0.0195 | NR* |

* Result may or may not be a false negative, depending on the participant's actual LOR.

### 6.6 Reporting of Additional Analytes

Three participants reported analytes that were not spiked into the test samples. These are presented in Table 15.

Table 15 Reported Results for Non-Spiked Analytes

| Lab. Code | Sample | Analyte | Result (mg/kg) | Uncertainty (mg/kg) | Recovery (%) |
|---|---|---|---|---|---|
| 1 | S2 | Dieldrin | 0.04 | NR | 80 |
| 5 | S2 | Glyphosate | 1.14 | 0.48 | NR |
| 24 | S2 | Cyfluthrin | 0.0153 | 0.0088 | NR |

Sample S2 was spiked with *trans*-chlordane and p,p'-DDE, and these analytes were scored. Seventeen participants also reported a total chlordane and total DDT value, which were not scored for this study. These results are presented in Tables 16 and 17 for information only.

Table 16 Reported Sample S2 Total Chlordane Results

| Lab. Code | Result (mg/kg) | Uncertainty (mg/kg) | Recovery (%) |
|---|---|---|---|
| 1 | 1 | 0.28 | NR |
| 3 | 0.28 | 0.084 | 70.7 |
| 4 | 0.49 | 0.25 | NR |
| 7 | 0.44 | 0.11 | NR |
| 10 | 0.56 | NR | NR |
| 11 | 0.365 | 0.127 | NR |
| 12 | 0.21 | 0.084 | NR |
| 13 | 0.506 | 0.15 | NR |
| 14 | 0.52 | 0.16 | 90 |
| 17 | 0.243 | 0.083 | NR |
| 18 | 0.31 | 0.16 | NR |
| 19 | 0.42 | 0.13 | NR |
| 20 | 0.49 | 0.15 | NR |
| 21 | 0.47 | 0.07 | NR |
| 22 | 0.45 | 32 | NR |
| 23 | 0.387 | 0.116 | NR |
| 24 | 0.44 | 0.14 | NR |

Table 17 Reported Sample S2 Total DDT Results

| Lab. Code | Result (mg/kg) | Uncertainty (mg/kg) | Recovery (%) |
|---|---|---|---|
| 1 | 1 | 0.25 | NR |
| 3 | 0.38 | 0.114 | 89.2 |
| 4 | 0.55 | 0.27 | NR |
| 7 | 0.49 | 0.11 | NR |
| 10 | 0.46 | NR | NR |
| 11 | 0.602 | 0.123 | NR |
| 12 | 0.32 | 0.13 | NR |
| 13 | 0.56 | 0.17 | NR |
| 14 | 0.75 | 0.23 | NR |
| 15 | 0.47 | 0.04 | NR |
| 17 | 0.244 | 0.083 | NR |
| 18 | 0.35 | 0.18 | NR |
| 19 | 0.47 | 0.14 | NR |
| 21 | 0.48 | 0.05 | NR |
| 22 | 0.44 | 32 | NR |
| 23 | 0.43 | 0.13 | NR |
| 24 | 0.45 | 0.23 | NR |

### 6.7 Range of Pesticides Analysed by Participants

Participants were provided with a list of potential analytes that could have been spiked into the test samples (Table 1). Of these analytes, seven were spiked into the samples for this study. Participants were not required to test for all potential analytes, and were requested to report “NT” (for “Not Tested”) for pesticides they did not analyse the samples for.

A summary of the participants’ testing of the spiked pesticides is presented in Table 18.

Laboratories **14** and **22** tested for all seven spiked pesticides. All participants tested for at least one of the spiked pesticides, with the proportion of pesticides analysed by each participant ranging from 14% to 100%.

Out of the spiked pesticides in this study, p,p’-DDE was analysed by the highest proportion of participants (91%). The proportion of participants analysing each pesticide in this study ranged from 32% to 91%.

Table 18 Summary of Pesticides Analysed by Participants

| Lab. Code | Bifenthrin | Cyfluthrin | Dieldrin | Glyphosate | Imidacloprid | p,p'-DDE | *trans*-Chlordane | Proportion of Analytes (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | NT | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | 86 |
| 3 | NT | ✓ | ✓ | NT | ✓ | ✓ | ✓ | 71 |
| 4 | NT | NT | ✓ | NT | NT | ✓ | ✓ | 43 |
| 5 | NT | NT | NT | ✓ | NT | NT | NT | 14 |
| 7 | ✓ | NT | ✓ | NT | NT | ✓ | ✓ | 57 |
| 8 | NT | NT | NT | NT | ✓ | NT | NT | 14 |
| 9 | ✓ | NT | ✓ | NT | NT | ✓ | ✓ | 57 |
| 10 | ✓ | ✓ | ✓ | NT | ✓ | ✓ | ✓ | 86 |
| 11 | ✓ | NT | ✓ | NT | NT | ✓ | ✓ | 57 |
| 12 | NT | NT | ✓ | ✓ | NT | ✓ | ✓ | 57 |
| 13 | NT | NT | NT | NT | ✓ | ✓ | ✓ | 43 |
| 14 | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | 100 |
| 15 | ✓ | ✓ | ✓ | NT | NT | ✓ | ✓ | 71 |
| 16 | ✓ | ✓ | ✓ | NT | NT | ✓ | NT | 57 |
| 17 | ✓ | ✓ | ✓ | ✓ | NT | ✓ | ✓ | 86 |
| 18 | ✓ | NT | ✓ | NT | ✓ | ✓ | ✓ | 71 |
| 19 | ✓ | ✓ | ✓ | NT | NT | ✓ | ✓ | 71 |
| 20 | NT | NT | ✓ | ✓ | NT | ✓ | ✓ | 57 |
| 21 | ✓ | NT | ✓ | NT | NT | ✓ | ✓ | 57 |
| 22 | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | 100 |
| 23 | NT | NT | ✓ | NT | NT | ✓ | ✓ | 43 |
| 24 | ✓ | ✓ | ✓ | NT | NT | ✓ | ✓ | 71 |
| Proportion of Participants (%) | 59 | 45 | 86 | 32 | 36 | 91 | 86 | 62 |

### 6.8 Participants' Analytical Methods

A variety of analytical methods were used for the different analytes (Appendix 3).

Participants used a sample size between 1 g and 30 g per analysis. There was no significant correlation overall between the results obtained and the sample mass used for analysis (Figure 12).

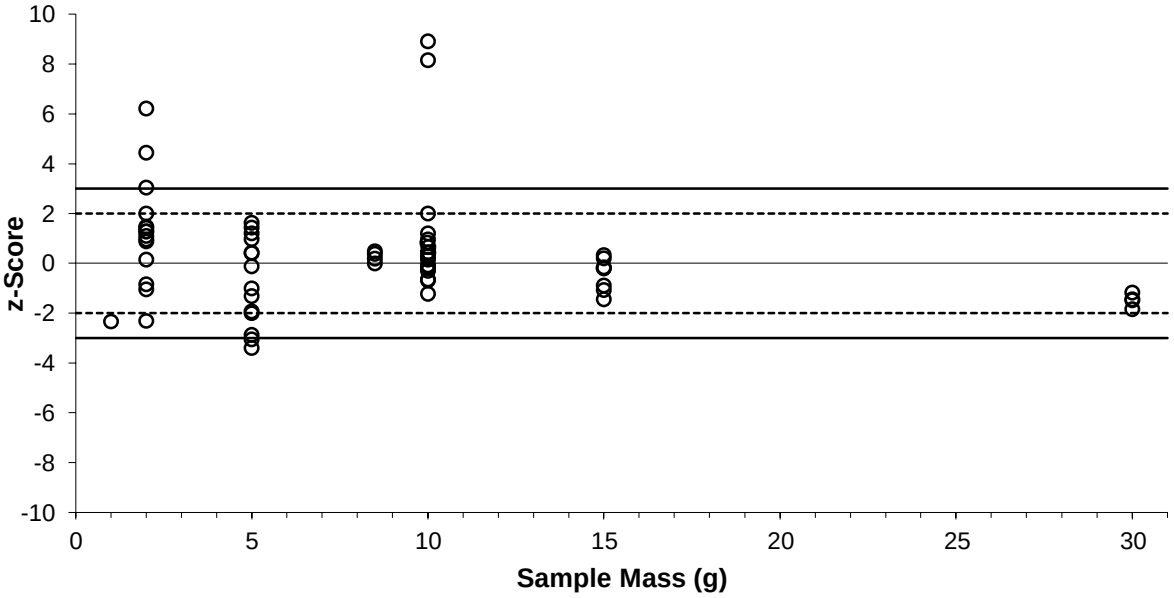



Figure 12 z-Score vs Sample Mass Used for Analysis

Participants used a variety of extraction techniques including solid-liquid extraction, QuEChERS and sonication. Participants used dichloromethane, acetone, ethyl acetate, hexane, acetonitrile, methanol, bases (including KOH and NaOH) and combinations of these as the extraction solvent. Six participants reported using a clean-up step for their analyses; these included using Florisil, d-SPE / QuEChERS, PSA/C18 and $Na_2SO_4$. Instruments employed by participants for the analysis of pesticides of interest in this study included LC-MS(MS), LC-Orbitrap, LC-DAD, HPLC-FLD, GC-MS(MS), and GC-ECD.

Plots of results reported and methodology used are presented in Figures 13 to 17 for scored analytes. Results are compared both by preparation techniques (left), and by measurement instrument used (right) for each analyte. Extraction technique abbreviations used in figures: QuEChERS = Quick, Easy, Cheap, Effective, Rugged, and Safe Extraction; SLE = Solid-Liquid Extraction. Solvent abbreviations used in figures: ACE = Acetone; ACN = Acetonitrile; DCM = Dichloromethane; EtOAc = Ethyl Acetate; HEX = Hexane; MeOH = Methanol. Instrument abbreviations used in figures: HPLC = High Performance Liquid Chromatography; LC = Liquid Chromatography; GC = Gas Chromatography; ECD = Electron Capture Detector; FLD = Fluorescence Detector; MS = Mass Spectrometry; MS/MS = Tandem Mass Spectrometry. If a participant did not report their methodology or instrument, this has been recorded as NR.

Due to the wide variety of methodologies employed, no significant trend was observed.

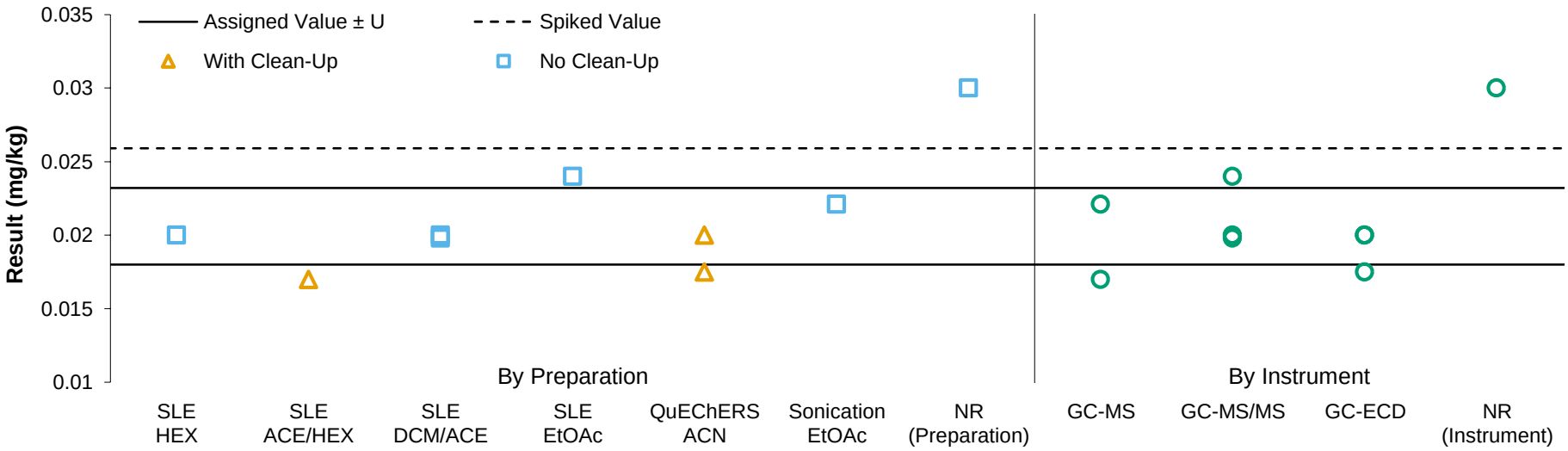



Figure 13 Sample S1 Bifenthrin Results vs Methodology

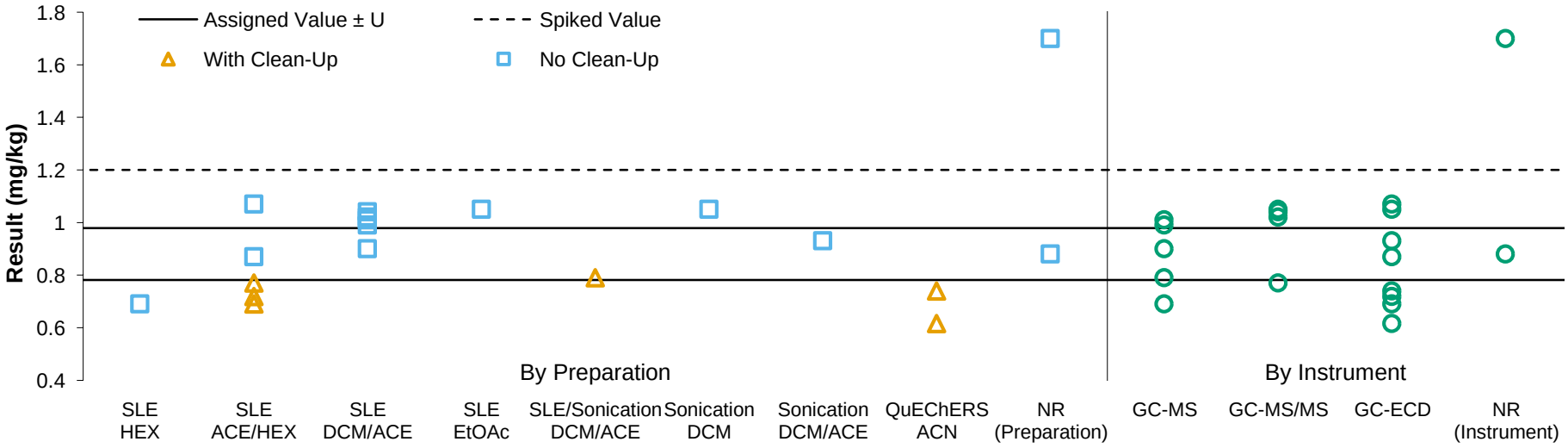



Figure 14 Sample S1 Dieldrin Results vs Methodology

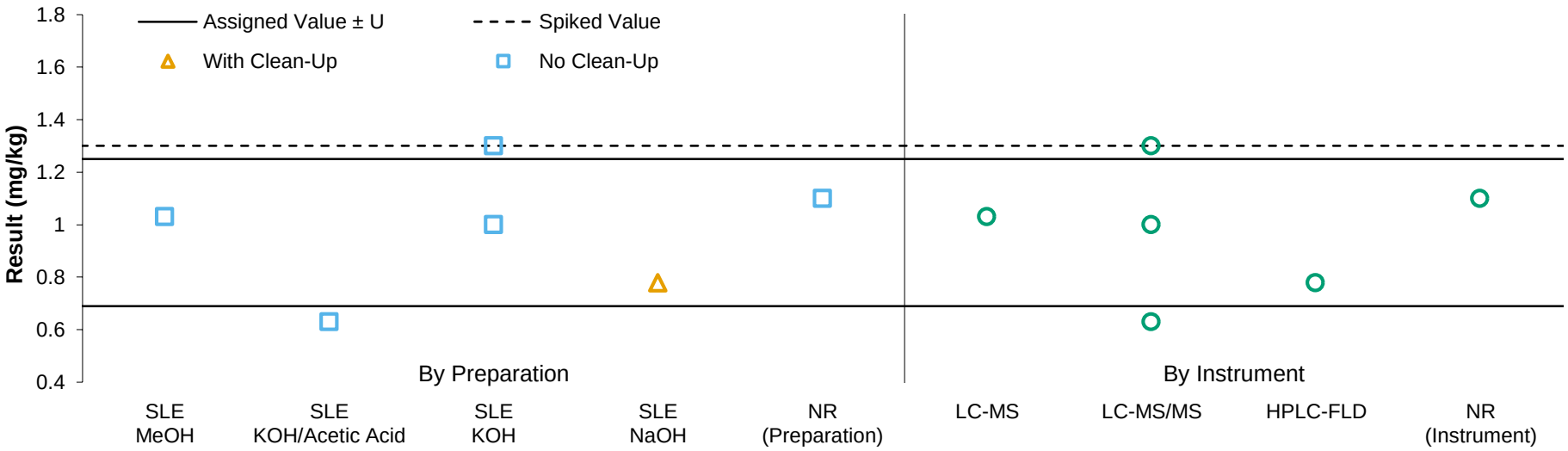



Figure 15 Sample S1 Glyphosate Results vs Methodology

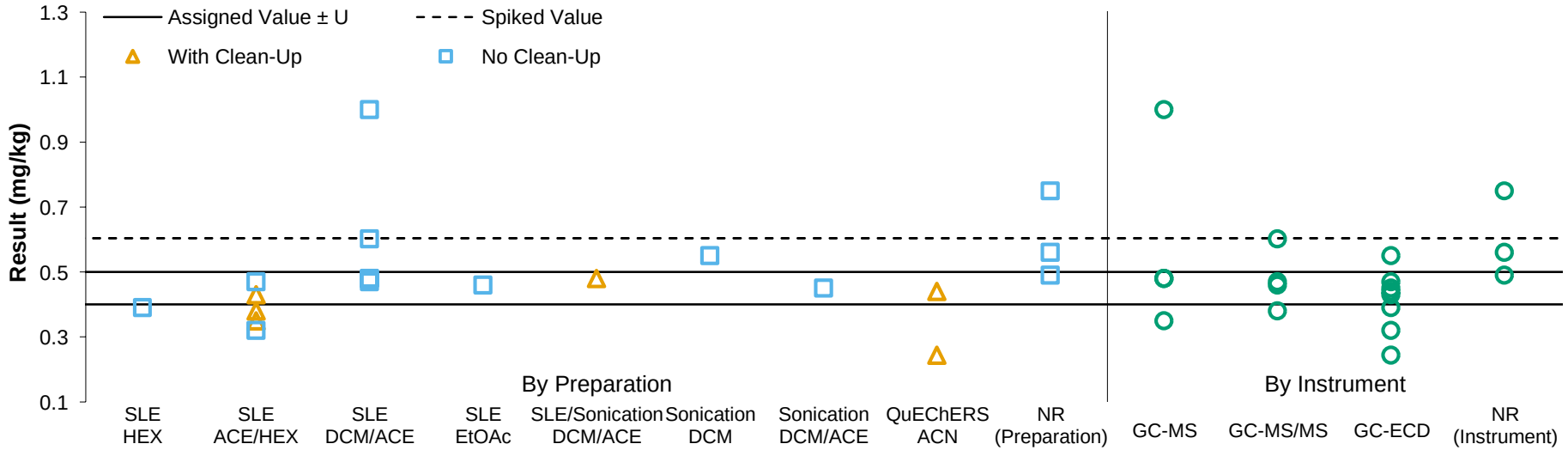



Figure 16 Sample S2 p,p'-DDE Results vs Methodology

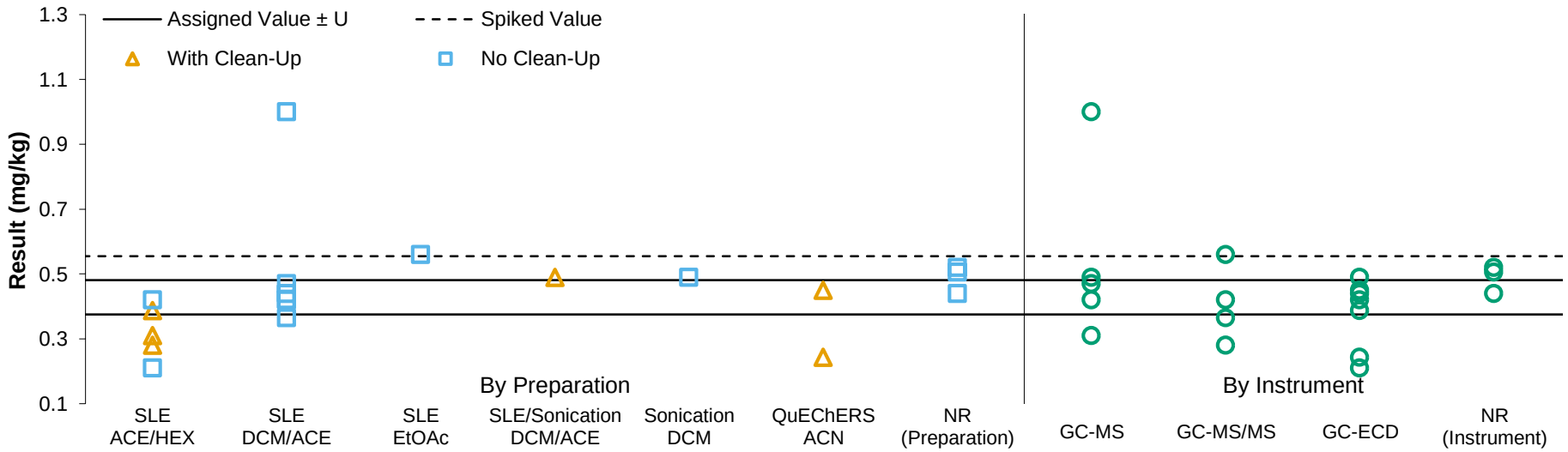



Figure 17 Sample S2 *trans*-Chlordane Results vs Methodology

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, corrected 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**, **3**, **8**, **9**, **10**, **12**, **14**, **16**, **17**, **18** and **22** reported recoveries for at least one analyte considered in this study, and the recoveries reported were in the range of 49% to 122%. Laboratories **13** and **14** reported that they corrected results for recovery.

### 6.9 Certified Reference Materials (CRM)

Participants were requested to indicate whether certified standards or matrix reference materials had been used as part of the quality assurance for their analysis. Sixteen participants reported using certified standards and two participants reported using matrix reference materials. The following were listed:

- Accustandard
- ChemLab
- ChemService
- Dr Ehrenstorfer
- ERA (e.g. CRM 728, CRM 727)
- o2si
- Restek
- Supelco (e.g. CRM47426, SQC009)
- ISO 17034 certified standards
- Custom pesticide standards

These materials may or may not meet the internationally recognised definition of a CRM:

> *'**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'*[11]

### 6.10 Summary of Participants' Results and Performances

Summaries of participants' results and performances for scored analytes in this PT study are presented in Table 19 and Figure 18.

Table 19 Summary of Participants' Results* (all results in mg/kg)

| Lab. Code | S1 Bifenthrin | S1 Dieldrin | S1 Glyphosate | S2 p,p'-DDE | S2 *trans*-Chlordane |
|---|---|---|---|---|---|
| A.V. | 0.0206 | 0.88 | 0.97 | 0.450 | 0.428 |
| S.V. | 0.0259 | 1.20 | 1.30 | 0.604 | 0.555 |
| 1 | NT | 0.9 | <0.01 | 1 | 1 |
| 3 | NT | 0.77 | NT | 0.38 | 0.28 |
| 4 | NT | 1.05 | NT | 0.55 | 0.49 |
| 5 | NT | NT | 0.63 | NT | NT |
| 7 | <0.05 | 0.88 | NT | 0.49 | 0.44 |
| 8 | NT | NT | NT | NT | NT |
| 9 | NR | 1.01 | NT | 0.48 | 0.42 |
| 10 | 0.024 | 1.05 | NT | 0.46 | 0.56 |
| 11 | 0.0198 | 1.02 | NT | 0.602 | 0.365 |
| 12 | NT | 1.07 | 1.03 | 0.32 | 0.21 |
| 13 | NT | NT | NT | 0.56 | 0.506 |
| 14 | 0.030 | 1.7 | 1.1 | 0.75 | 0.52 |
| 15 | <0.2 | 0.87 | NT | 0.47 | 0.42 |
| 16 | 0.02 | 0.69 | NT | 0.39 | NT |
| 17 | 0.0175 | 0.616 | 0.779 | 0.244 | 0.243 |
| 18 | 0.017 | 0.69 | NT | 0.35 | 0.31 |
| 19 | 0.02 | 1.04 | NT | 0.47 | 0.42 |
| 20 | NT | 0.79 | 1.3 | 0.48 | 0.49 |
| 21 | < 0.05 | 0.99 | NT | 0.48 | 0.47 |
| 22 | 0.02 | 0.74 | 1.0 | 0.44 | 0.45 |
| 23 | NT | 0.719 | NT | 0.43 | 0.387 |
| 24 | 0.0221 | 0.93 | NT | 0.45 | 0.44 |

* Shaded cells are results which returned a questionable or unsatisfactory z-score. A.V. = Assigned Value; S.V. = Spiked Value.

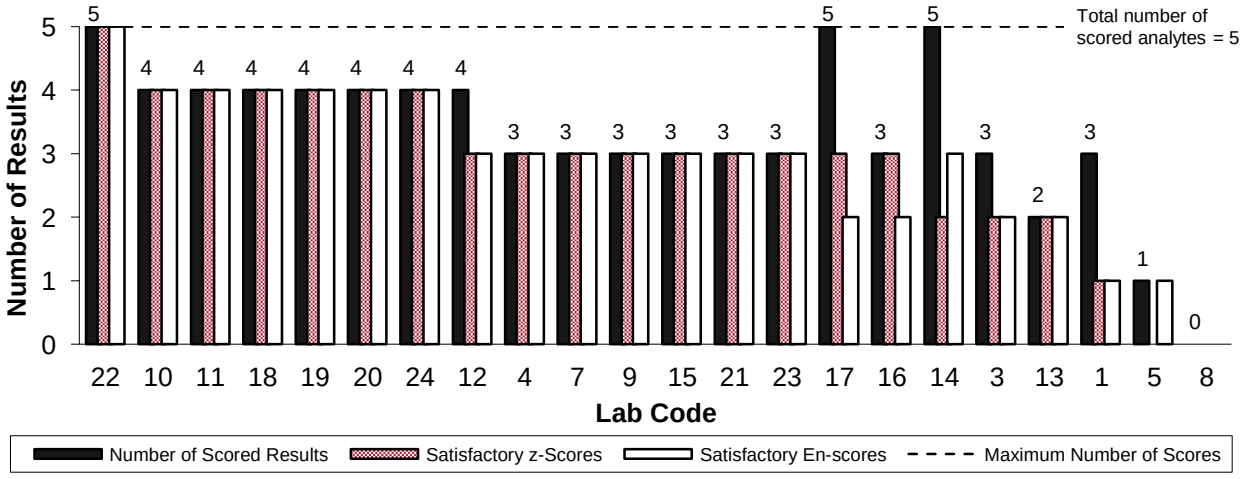



Figure 18 Summary of Participants' Performance

### 6.11 Comparison with Previous Pesticides in Soil PT Studies

A summary of participation and reported results rates in Pesticides in Soil PT studies over the last 10 studies (2013 – 2021) is presented in Figure 19.

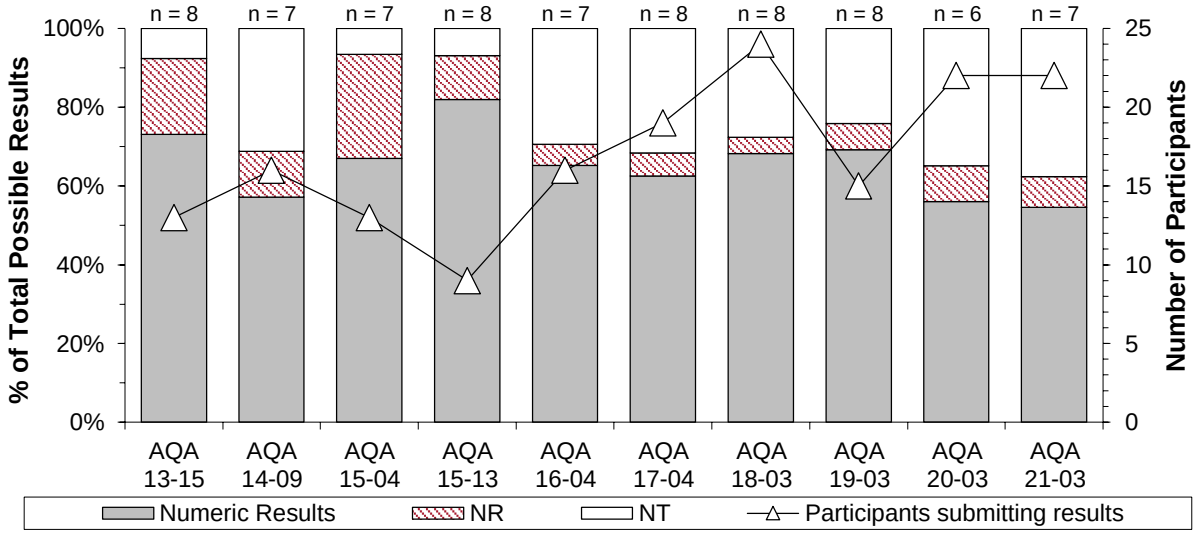



Figure 19 Summary of Participation and Reported Results in Pesticides in Soil PT Studies (n = number of spiked analytes)

A summary of the satisfactory performance (presented as a percentage of the total number of scores for each study) obtained by participants in Pesticides in Soil PT studies over the last 10 studies (2013 – 2021) is presented in Figure 20. To enable direct comparison, the target SD used to calculate z-scores has been kept constant at 15% PCV. Over this period, the average proportion of satisfactory z-scores and $E_n$-scores was 81% for both. While each proficiency testing study has a different sample set and a different group of participant laboratories, taken as a group, the performance over this period has improved.

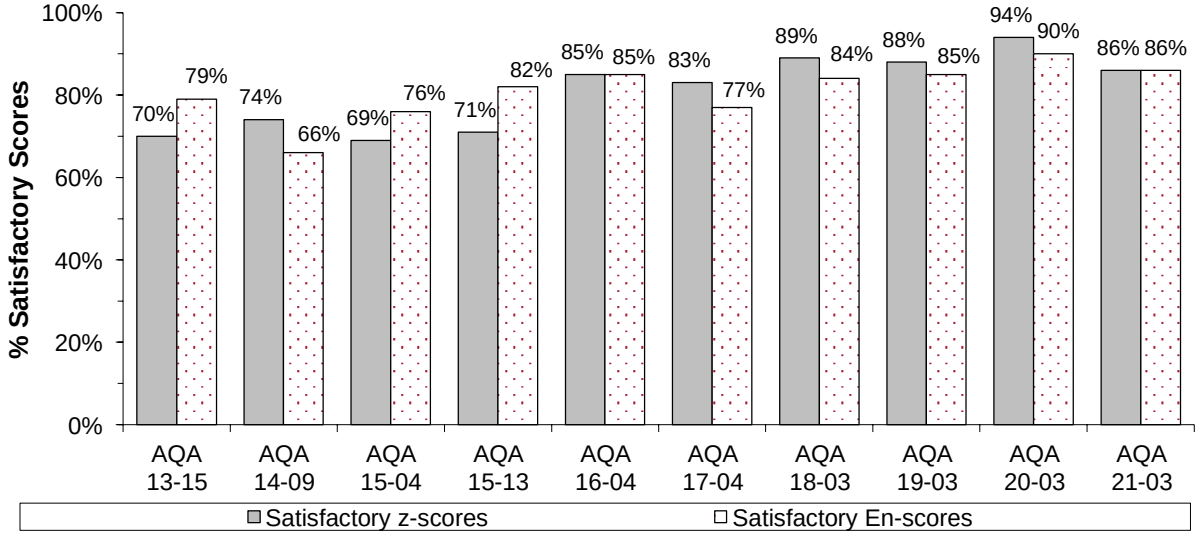



Figure 20 Satisfactory z-Scores and $E_n$-Scores in Pesticides in Soil PT Studies

Individual performance history reports are emailed to participants at the end of each study; the consideration of z-scores over time provides much more useful information than a single score. Over time, laboratories should expect at least 95% of their 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 method or laboratory bias.

## 7 REFERENCES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[4] Thompson, M., Ellison, S.L.R. & Wood, R., 2006, 'The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories', *Pure Appl. Chem.*, vol. 78, pp. 145-196.

[5] National Environmental Protection (Assessment of Site Contamination) Measure 1999 as amended 2013, Volume 2: Schedule B1, *Guideline on Investigation Levels for Soil and Groundwater,* viewed June 2021, <https://www.legislation.gov.au/Details/F2013C00288/Html/Volume_2>.

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[9] ISO/IEC 17025:2017, *General requirements for the competence of testing and calibration laboratories.*

[10] Eurachem/CITAC Guide GC 4, QUAM:2012.P1, *Quantifying Uncertainty in Analytical Measurement*, 3rd edition, viewed June 2021, <http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf>.

[11] JCGM 200:2012, *International vocabulary of metrology – Basic and general concepts and associated terms (VIM)*, 3rd edition.

## APPENDIX 1 – SAMPLE PREPARATION

Forty bottles of each of Sample S1 and Sample S2 were prepared using dried, ground and sieved Australian Native Landscapes Menangle topsoil. The 350 µm to 850 µm fraction was used to prepare the samples.

**Sample S1** was prepared by weighing 2236.0 g of soil into a stainless steel drum, adding acetone to cover the soil, and allowing it to be stirred. The stirred soil suspension was spiked with the pesticide standard solutions. The solvent was allowed to evaporate off in a fume cupboard. After drying, the soil was divided using a Retsch sample divider and dispensed into 65 mL glass jars.

**Sample S2** was prepared by weighing 2210.8 g of soil into a stainless steel drum, adding acetone to cover the soil, and allowing it to be stirred. The stirred soil suspension was spiked with the pesticide standard solutions. The solvent was allowed to evaporate off in a fume cupboard. After drying, the soil was divided using a Retsch sample divider and dispensed into 65 mL glass jars.

## APPENDIX 2 – TRANSPORTATION STABILITY ASSESSMENT

Samples were refrigerated at 4 °C after preparation and prior to dispatch. For dispatch, samples were packaged into insulated foam boxes with cooler bricks.

Comparisons of results obtained to days spent in transit for scored analytes are presented in Figures 21 to 25. No evidence of analyte degradation with respect to the amount of time spent in transit was observed. For Sample S1 glyphosate, NMI performed an additional stability assessment by analysing a sample left at room temperature for 6 days (equivalent to the maximum transit time for participants reporting results for this analyte); it was also found that there was no evidence of degradation for this analyte over this time period.

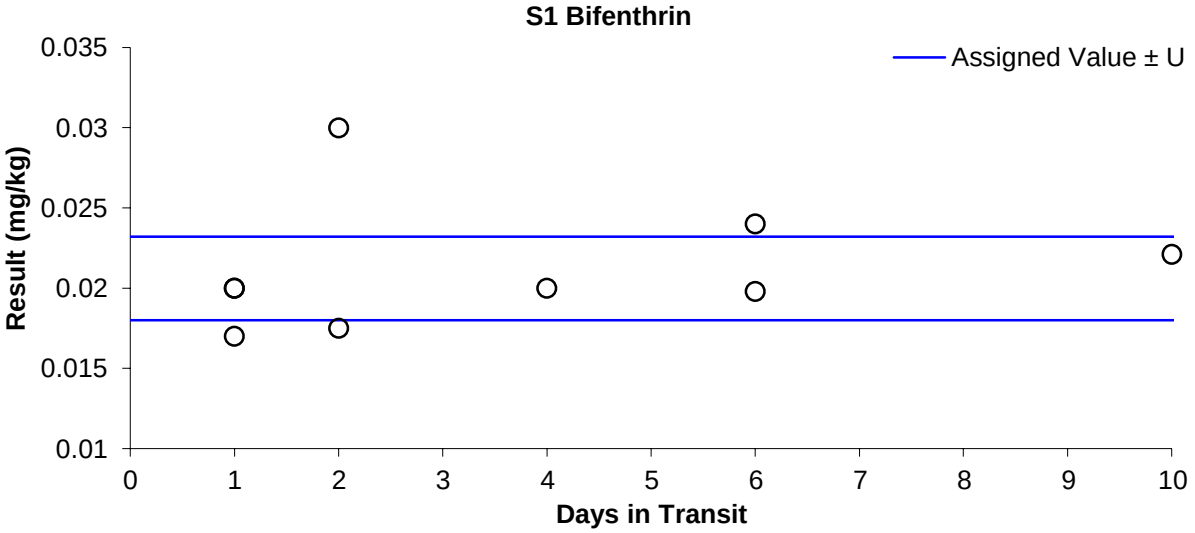


Figure 21 Sample S1 Bifenthrin Results vs Days in Transit

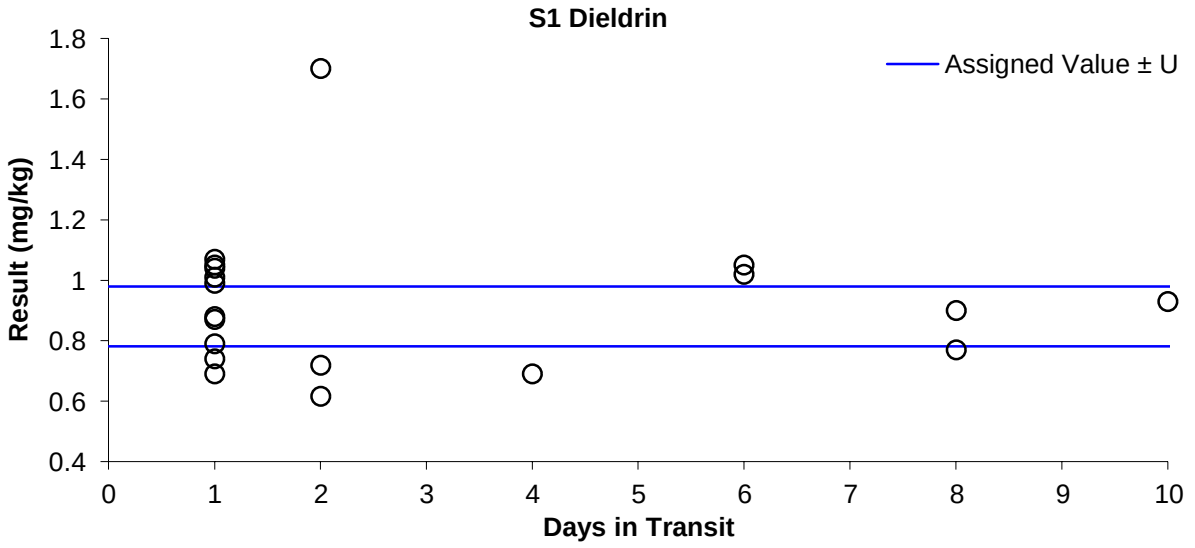


Figure 22 Sample S1 Dieldrin Results vs Days in Transit

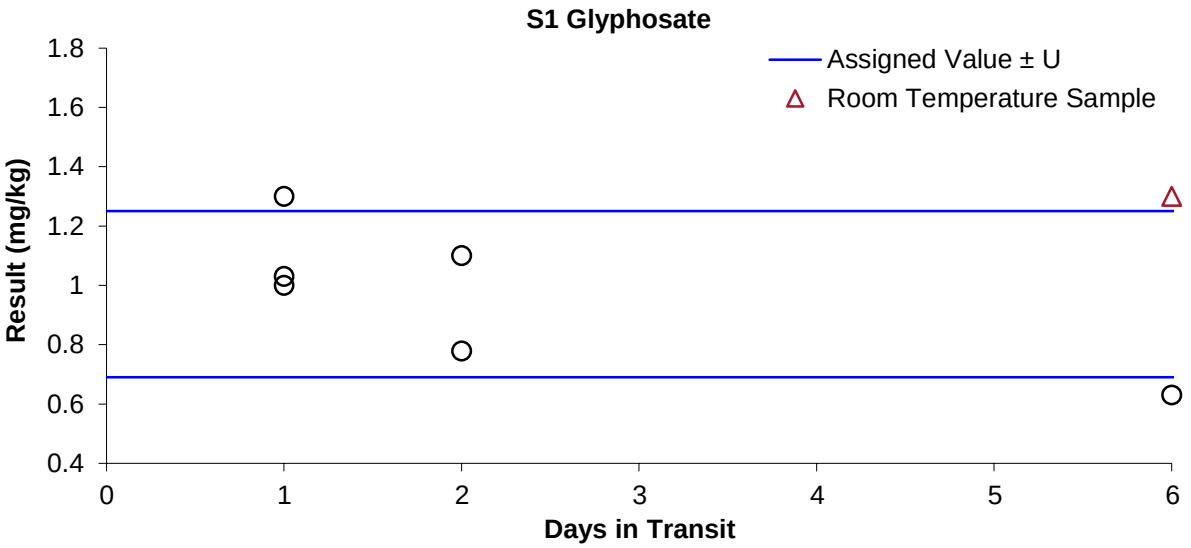


Figure 23 Sample S1 Glyphosate Results vs Days in Transit

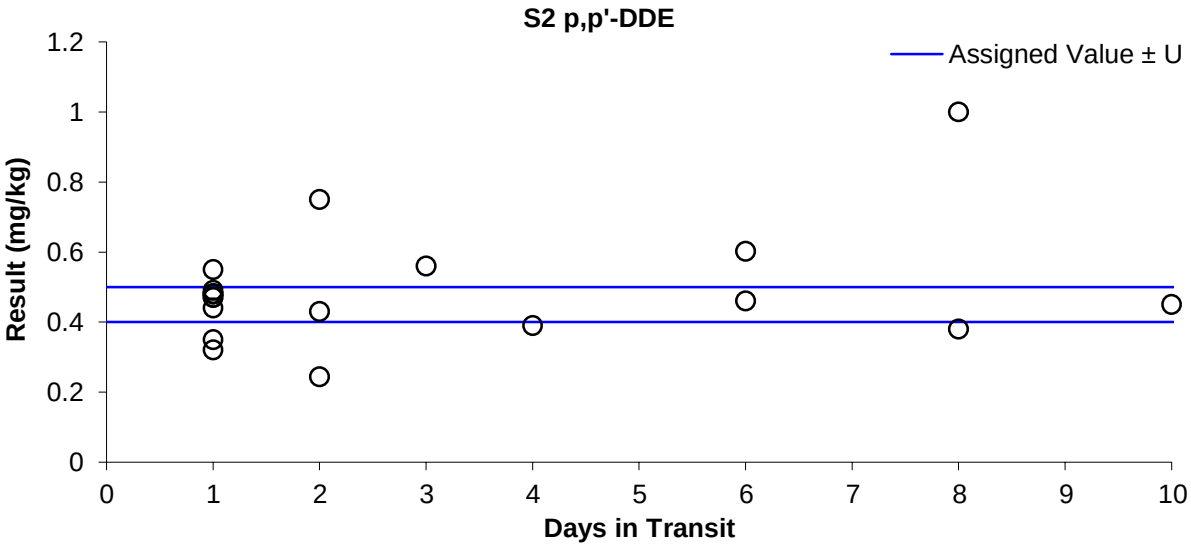


Figure 24 Sample S2 p,p'-DDE Results vs Days in Transit

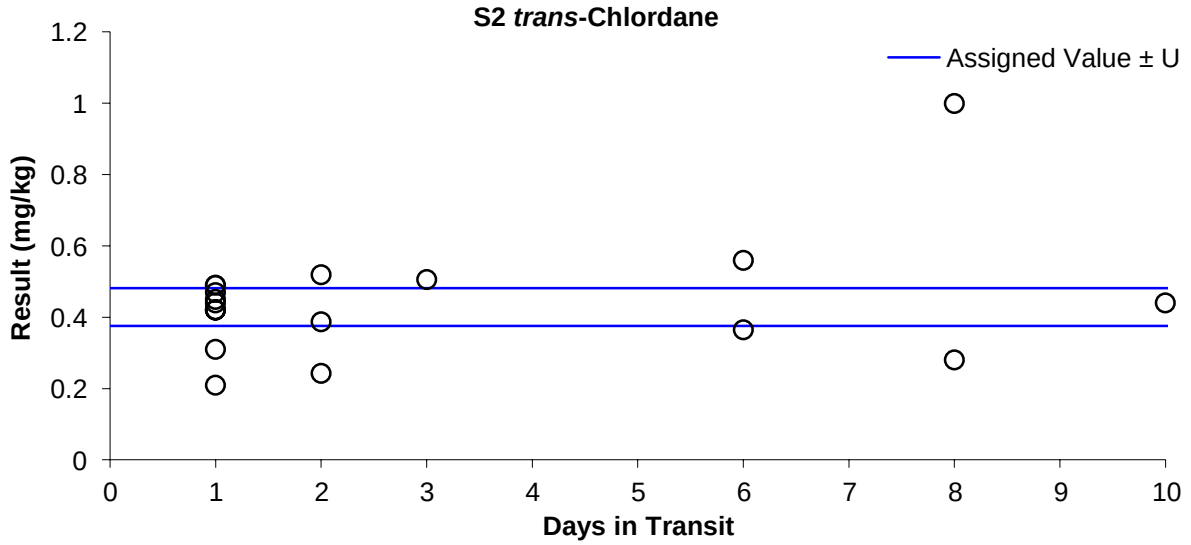


Figure 25 Sample S2 *trans*-Chlordane Results vs Days in Transit

## APPENDIX 3 – TEST METHODS REPORTED BY PARTICIPANTS

Participants were requested to provide information about their test methods. Responses are presented in Tables 20 to 27. Some responses may be modified so that the participant cannot be identified.

Table 20 Sample Mass Used for Analysis

| Lab. Code | S1 Sample Mass (g) | S2 Sample Mass (g) |
|---|---|---|
| 1 | 10<br>(2g extracted for LC-MS/MS analysis) | 10<br>(2g extracted for LC-MS/MS analysis) |
| 3 | 2 | 2 |
| 4 | 2 | 2 |
| 5 | 1 | 1 |
| 7 | | |
| 8 | | |
| 9 | 5 | 5 |
| 10 | 2 | 2 |
| 11 | | |
| 12 | 5 | 5 |
| 13 | 5 | 5 |
| 14 | 2 | 2 |
| 15 | 10 | 10 |
| 16 | 15 | 15 |
| 17 | 5 | 5 |
| 18 | 55<br>(30g sample used for GC-MS analysis; 25 g used for LC-Orbitrap analysis) | 55<br>(30g sample used for GC-MS analysis; 25 g used for LC-Orbitrap analysis) |
| 19 | 10<br>(5 g of sample used for LC-DAD analysis) | 10<br>(5 g of sample used for LC-DAD analysis) |
| 20 | 10 | 10 |
| 21 | 9.99 | 10.01 |
| 22 | 15 | 15 |
| 23 | 10 | 10 |
| 24 | 8.5 | 8.5 |

Table 21 Test Methods Bifenthrin

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|
| 1 | NT | | | |
| 3 | NT | | | |
| 4 | NT | | | |
| 5 | NT | | | |
| 7 | | | | |
| 8 | NT | | | |
| 9 | Solid-Liquid | 1:1 DCM:Acetone | None | GC-MS |
| 10 | Solid-Liquid | EtAc | | GC-MS/MS |
| 11 | Solid-Liquid | DCM,Acetone | | GC-MS/MS |
| 12 | NT | | | |
| 13 | NT | | | |
| 14 | | | | |
| 15 | Solid-Liquid | Acetone:Hexane | Nil | GC-ECD |
| 16 | Solid-Liquid | Hexane | None | GC-ECD |
| 17 | QuEChERS | Acetonitrile | d-SPE | GC-ECD |
| 18 | Solid-Liquid | Acetone/Hexane | Florisil | GC-MS |
| 19 | Solid-Liquid | DCM/ACE (1:1) | N/A | GC-MS/MS |
| 20 | NT | | | |
| 21 | Solid-Liquid | DCM /Acetone | None | GC-MS |
| 22 | QuEChERS | ACN 1% acetic acid | PSA / C18 | GC-ECD |
| 23 | NT | | | |
| 24 | Sonication | Ethyl Acetate | NIL | GC-MS |

Table 22 Test Methods Cyfluthrin

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|
| 1 | Solid-Liquid | DCM:acetone | | GC-MS |
| 3 | QuEChERS | acetonitrile | NA | LC-MS/MS |
| 4 | NT | | | |
| 5 | NT | | | |
| 7 | NT | | | |
| 8 | NT | | | |
| 9 | NT | | | |
| 10 | Solid-Liquid | EtAc | | GC-MS/MS |
| 11 | NT | | | |
| 12 | NT | | | |
| 13 | NT | | | |
| 14 | | | | |
| 15 | Solid-Liquid | Acetone:Hexane | Nil | GC-ECD |
| 16 | Solid-Liquid | Hexane | None | GC-ECD |
| 17 | QuEChERS | Acetonitrile | d-SPE | GC-ECD |
| 18 | NT | | | |
| 19 | Solid-Liquid | MeCN | N/A | LC-DAD |
| 20 | NT | | | |
| 21 | NT | | | |
| 22 | QuEChERS | ACN 1% acetic acid | PSA / C18 | GC-ECD |
| 23 | NT | | | |
| 24 | Sonication | Ethyl Acetate | NIL | GC-MS |

Table 23 Test Methods Dieldrin

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|
| 1 | Solid-Liquid | DCM:acetone | | GC-MS |
| 3 | Solid-Liquid | acetone-hexane | Florisil | GC-MS/MS |
| 4 | Sonication | DCM Extraction | None | GC-ECD |
| 5 | NT | | | |
| 7 | | | | |
| 8 | NT | | | |
| 9 | Solid-Liquid | 1:1 DCM:Acetone | None | GC-MS |
| 10 | Solid-Liquid | EtAc | | GC-MS/MS |
| 11 | Solid-Liquid | DCM,Acetone | | GC-MS/MS |
| 12 | Solid-Liquid | Acetone/hexane | | GC-ECD |
| 13 | NT | | | |
| 14 | | | | |
| 15 | Solid-Liquid | Acetone:Hexane | Nil | GC-ECD |
| 16 | Solid-Liquid | Hexane | None | GC-ECD |
| 17 | QuEChERS | Acetonitrile | d-SPE | GC-ECD |
| 18 | Solid-Liquid | Acetone/Hexane | Florisil | GC-MS |
| 19 | Solid-Liquid | DCM/ACE (1:1) | N/A | GC-MS/MS |
| 20 | Solid-Liquid, sonication | DCM:Acetone | filter through NaSO4 | GC-MS |
| 21 | Solid-Liquid | DCM /Acetone | None | GC-MS |
| 22 | QuEChERS | ACN 1% acetic acid | PSA / C18 | GC-ECD |
| 23 | Solid-Liquid | Hexane:Acetone | Sulfur | GC-ECD |
| 24 | Sonication | DCM:Acetone 1:1 | NIL | GC-ECD |

Table 24 Test Methods Glyphosate

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|
| 1 | QuEChERS | MeOH | | LC-MS/MS |
| 3 | NT | | | |
| 4 | NT | | | |
| 5 | Solid-Liquid | KOH, Acetic acid | No | LC-MS/MS |
| 7 | NT | | | |
| 8 | NT | | | |
| 9 | NT | | | |
| 10 | NT | | | |
| 11 | NT | | | |
| 12 | Solid-Liquid | Methanol | | LC-MS |
| 13 | NT | | | |
| 14 | | | | |
| 15 | NT | | | |
| 16 | NT | | | |
| 17 | Solid-Liquid | 1 N NaOH | Resin | HPLC/FLD Post-column derivatizer |
| 18 | NT | | | |
| 19 | NT | | | |
| 20 | Solid-Liquid | aqueous KOH | | LC-MS/MS |
| 21 | NT | | | |
| 22 | Solid-Liquid | 0.6M KOH | None | LC-MS/MS |
| | FMOC derivatization | | | |
| 23 | NT | | | |
| 24 | NT | | | |

Table 25 Test Methods Imidacloprid

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|
| 1 | QuEChERS | ACN | | LC-MS/MS |
| 3 | QuEChERS | acetonitrile | NA | LC-MS/MS |
| 4 | NT | | | |
| 5 | NT | | | |
| 7 | NT | | | |
| 8 | ASE extraction | 90%MeCN:10% H2O | | LC-MS/MS |
| 9 | NT | | | |
| 10 | Solid-Liquid | EtAc | | GC-MS/MS |
| 11 | NT | | | |
| 12 | NT | | | |
| 13 | | | | |
| 14 | | | | |
| 15 | NT | | | |
| 16 | NT | | | |
| 17 | NT | | | |
| 18 | Solid-Liquid | Acetone | QuEChERS | LC-Orbitrap |
| 19 | NT | | | |
| 20 | NT | | | |
| 21 | NT | | | |
| 22 | QuEChERS | ACN 1% acetic acid | PSA / C18 | LC-MS/MS |
| 23 | NT | | | |
| 24 | NT | | | |

Table 26 Test Methods p,p’-DDE

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|
| 1 | Solid-Liquid | DCM:acetone | | GC-MS |
| 3 | Solid-Liquid | acetone-hexane | Florisil | GC-MS/MS |
| 4 | Sonication | DCM Extraction | None | GC-ECD |
| 5 | NT | | | |
| 7 | | | | |
| 8 | NT | | | |
| 9 | Solid-Liquid | 1:1 DCM:Acetone | None | GC-MS |
| 10 | Solid-Liquid | EtAc | | GC-MS/MS |
| 11 | Solid-Liquid | DCM,Acetone | | GC-MS/MS |
| 12 | Solid-Liquid | Acetone/hexane | | GC-ECD |
| 13 | | | | |
| 14 | | | | |
| 15 | Solid-Liquid | Acetone:Hexane | Nil | GC-ECD |
| 16 | Solid-Liquid | Hexane | None | GC-ECD |
| 17 | QuEChERS | Acetonitrile | d-SPE | GC-ECD |
| 18 | Solid-Liquid | Acetone/Hexane | Florisil | GC-MS |
| 19 | Solid-Liquid | DCM/ACE (1:1) | N/A | GC-MS/MS |
| 20 | Solid-Liquid, sonication | DCM:Acetone | filter through NaSO4 | GC-MS |
| 21 | Solid-Liquid | DCM /Acetone | None | GC-MS |
| 22 | QuEChERS | ACN 1% acetic acid | PSA / C18 | GC-ECD |
| 23 | Solid-Liquid | Hexane:Acetone | Sulfur | GC-ECD |
| 24 | Sonication | DCM:Acetone 1:1 | NIL | GC-ECD |

Table 27 Test Methods *trans*-Chlordane

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|
| 1 | Solid-Liquid | DCM:acetone | | GC-MS |
| 3 | Solid-Liquid | acetone-hexane | Florisil | GC-MS/MS |
| 4 | Sonication | DCM Extraction | None | GC-ECD |
| 5 | NT | | | |
| 7 | | | | |
| 8 | NT | | | |
| 9 | Solid-Liquid | 1:1 DCM:Acetone | None | GC-MS |
| 10 | Solid-Liquid | EtAc | | GC-MS/MS |
| 11 | Solid-Liquid | DCM,Acetone | | GC-MS/MS |
| 12 | Solid-Liquid | Acetone/hexane | | GC-ECD |
| 13 | | | | |
| 14 | | | | |
| 15 | Solid-Liquid | Acetone:Hexane | Nil | GC-ECD |
| 16 | NT | | | |
| 17 | QuEChERS | Acetonitrile | d-SPE | GC-ECD |
| 18 | Solid-Liquid | Acetone/Hexane | Florisil | GC-MS |
| 19 | Solid-Liquid | DCM/ACE (1:1) | N/A | GC-MS/MS |
| 20 | Solid-Liquid, sonication | DCM:Acetone | filter through NaSO4 | GC-MS |
| 21 | Solid-Liquid | DCM /Acetone | None | GC-MS |
| 22 | QuEChERS | ACN 1% acetic acid | PSA / C18 | GC-ECD |
| 23 | Solid-Liquid | Hexane:Acetone | Sulfur | GC-ECD |
| 24 | Solid-Liquid | DCM:Acetone 1:1 | NIL | GC-ECD |

## APPENDIX 4 – ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY, Z-SCORE AND $E_N$-SCORE CALCULATIONS

### A4.1 Robust Average and Associated Uncertainty

Robust averages were calculated using the procedure described in ISO 13528:2015.[7] The associated uncertainties were estimated as according to Equation 4.

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

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 for bifenthrin in Sample S1 is set out below in Table 28.

Table 28 Uncertainty of the Robust Average for Bifenthrin in Sample S1

| | |
|---|---|
| No. results (p) | 9 |
| Robust Average | 0.0206 mg/kg |
| $S_{rob\ av}$ | 0.0031 mg/kg |
| $u_{rob\ av}$ | 0.00129 mg/kg |
| $k$ | 2 |
| $U_{rob\ av}$ | 0.00258 mg/kg |

Therefore, the robust average for bifenthrin in Sample S1 is 0.0206 ± 0.0026 mg/kg.

### A4.2 z-Score and $E_n$-Score Calculations

For each participant's result, a z-score and $E_n$-score are calculated according to Equations 2 and 3 respectively.

A worked example is set out below in Table 29.

Table 29 z-Score and $E_n$-Score Calculation for Sample S1 Bifenthrin Result Reported by Laboratory 10

| Participant Result (mg/kg) | Assigned Value (mg/kg) | Target SD | z-Score | $E_n$-Score |
|---|---|---|---|---|
| 0.024 ± 0.012 | 0.0206 ± 0.0026 | 15% as PCV, or: 0.15 × 0.0206 = 0.00309 mg/kg | z-Score = $\frac{0.024-0.0206}{0.00309}$ = 1.10 | $E_n$-Score = $\frac{0.024-0.0206}{\sqrt{0.012^2+0.0026^2}}$ = 0.28 |

## APPENDIX 5 – ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| 2,4-D | 2,4-Dichlorophenoxyacetic acid |
| A.V. | Assigned Value |
| ACE | Acetone |
| ACN | Acetonitrile |
| CITAC | Cooperation on International Traceability in Analytical Chemistry |
| CRM | Certified Reference Material |
| CV | Coefficient of Variation |
| DAD | Diode Array Detector |
| DCM | Dichloromethane |
| d-SPE | Dispersive Solid Phase Extraction |
| ECD | Electron Capture Detector |
| EtOAc | Ethyl Acetate |
| FLD | Fluorescence Detector |
| GAG | General Accreditation Guidance (NATA) |
| 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 |
| LOR | Limit Of Reporting |
| Max. | Maximum value in a set of results |
| MCPA | 2-methyl-4-chlorophenoxyacetic acid |
| Md | Median |
| MeOH | Methanol |
| Min. | Minimum value in a set of results |
| MS | Mass Spectrometry |
| MSMS | Tandem Mass Spectrometry |
| MU | Measurement Uncertainty |
| N | Number of numeric results |
| NATA | National Association of Testing Authorities, Australia |
| NMI | National Measurement Institute (Australia) |
| NR | Not Reported |
| NT | Not Tested |
| p,p'-DDD | Dichlorodiphenyldichloroethane |
| p,p'-DDE | Dichlorodiphenyldichloroethylene |
| p,p'-DDT | Dichlorodiphenyltrichloroethane |

| | |
|---|---|
| PCV | Performance Coefficient of Variation |
| PSA | Primary-Secondary Amine |
| PT | Proficiency Test |
| QuEChERS | Quick, Easy, Cheap, Effective, Rugged, and Safe preparation method |
| R.A. | Robust Average |
| RM | Reference Material |
| S.V. | Spiked Value |
| SD | Standard Deviation |
| SLE | Solid-Liquid Extraction |
| SS | Spiked Samples |
| Total DDT | Sum of DDD, DDE and DDT compounds |

**END OF REPORT**