Australian Government
Department of Industry, Science and Resources

National Measurement Institute

# Proficiency Test Final Report AQA 24-05A Pesticides in Fruit and Vegetables

October 2024

This report replaces AQA 24-05.

## REVISION HISTORY

| Date | Report Number | Reason for review |
|---|---|---|
| October 2024 | AQA 24-05 | Final Report – Original issue. |
| October 2024 | AQA 24-05A | Updated Sample S3 maleic hydrazide result for Laboratory **4** from 'NR' to 'NT' in Section 5. |

## ACKNOWLEDGMENTS

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

Jenny Xu

Geoff Morschel

Jasmine Duong

Luminita Antin

Aaron Mamo

Shobhna Chandra

Lesley Johnston

Annmaree Kenny

Toby Funston

Hao Nguyen

Jason Lu

Paul Adorno

Raluca Iavetz

Manager, Chemical Reference Values

105 Delhi Rd, North Ryde, NSW 2113, Australia

Phone: +61 2 9449 0178

Email: raluca.iavetz@measurement.gov.au


Accredited for compliance with ISO/IEC 17043

## TABLE OF CONTENTS

## SUMMARY

AQA 24-05 Pesticides in Fruit and Vegetables commenced in April 2024. Sixteen laboratories registered to participate, and all participants submitted results.

Three test samples were prepared at the NMI laboratory in Sydney. Samples were prepared by adding pesticide standard solutions to pureed tomatoes (Sample S1), plum (Sample S2) and garlic (Sample S3).

Of a possible 240 results, 165 numeric results (69%) were submitted. Of the remaining results, 13 results were a 'less than' value (< *x*) or Not Reported (NR), and 62 results were Not Tested (NT).

The assigned values for Sample S2 acephate, deltamethrin, endosulfan sulfate and imidacloprid were the reference values obtained using IDMS.

**Traceability:** The reference values are traceable to the SI unit for mass (kg) through the Australian national standards for mass and the certified reference materials used as the reference standards.

The assigned values for all other 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 pesticides in fruit and vegetables.*

Laboratories **3**, **4**, **7**, **10**, **11**, **16** reported numeric results for all 13 scored analytes.

Seven participants (Laboratories **3**, **6**, **10**, **12**, **13**, **14** and **15**) did not report results for analytes that they tested for and were present in the test samples (total of eight results).

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

Of 159 results for which *z*-scores were calculated, 117 (74%) returned $|z| \leq 2.0$, indicating an acceptable performance.

Of 159 results for which $E_n$-scores were calculated, 118 (74%) returned $|E_n| < 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratory **16** achieved acceptable *z*-scores and $E_n$-scores for all scored analytes.

- *Assess the ability of participants to determine compliance of pesticides in fruit and vegetables against regulatory standards.*

One regulatory standard in Australia is the Australia New Zealand Food Standards Code, which specifies maximum residue limits for various pesticides in different food products.

Of 64 results assessed, 55 (86%) gave the correct compliance status with respect to the Australia New Zealand Food Standards Code.

Laboratories **3**, **4**, **11** and **16** returned the correct compliance status for all assessed analytes.

- *Evaluate the participants' methods for the measurement of pesticides in fruit and vegetables.*

Participants used a variety of methods, and no significant trends with any particular sample preparation method or instrumental technique were evident. The most common methodology was extraction using the QuEChERS procedure, with acetonitrile as the extraction solvent and using GC-MS/MS or LC-MS/MS for analysis.

- *Develop the practical application of traceability and measurement uncertainty.*

Four analytes in this study had assigned values as reference values traceable to SI.

Of 165 numeric results for the analytes of interest in this study, 163 (99%) were reported with an associated expanded measurement uncertainty. The magnitude of the reported uncertainties was within the range 2.5% to 320% relative. A wide variety of procedures were used to estimate uncertainty.

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

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

NMI also has certified reference material MX030 Pesticides in Tomato Puree available for purchase.

# 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 interlaboratory comparisons'.[1] NMI PT studies target chemical testing in areas of high public significance such as trade, environment, law enforcement and food safety. NMI offers PT studies in:

- pesticide residues in soil, water, fruit, vegetables and herbs;
- hydrocarbons, phenols and volatile organic compounds in soil and water;
- inorganic analytes in soil, water, filters, food and pharmaceuticals;
- per- and polyfluoroalkyl substances in soil, biosolid, water, biota and food;
- controlled drug assay, drugs in wipes and clandestine laboratory; and
- allergens in food.

## 1.2 Study Aims

The aims of the study were to:

- assess the ability of participants to correctly identify pesticides in fruit and vegetables;
- compare the performances of participants and assess their accuracy in the measurement of pesticides in fruit and vegetables;
- assess the ability of participants to determine compliance of pesticides in fruit and vegetables against regulatory standards;
- evaluate participants' methods for the measurement of pesticides in fruit and vegetables;
- develop the practical application of traceability and measurement uncertainty; 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 17043:2023 as a provider of PT schemes.[1] This PT study is within the scope of NMI's accreditation.

## 2 STUDY INFORMATION

### 2.1 Study Timetable

The timetable of the study was:

Invitations sent 2/04/2024

Samples sent 29/04/2024

Results due 11/06/2024

Interim Report 13/06/2024

Preliminary Report 21/06/2024

The timeline for the release of the Final Report was extended as reference values were obtained for Sample S2 analytes.

### 2.2 Participation and Laboratory Code

Sixteen laboratories registered to participate, and all participants were assigned a confidential laboratory code number for this study. All participants submitted results.

### 2.3 Selection of Pesticides and Matrices

For pesticide and matrix selection, consideration was given to:

- a variety of pesticides amenable to gas and/or liquid chromatography;
- a variety of matrices, and the availability of matrix material with incurred analytes;
- feedback from participants and other stakeholders;
- current Australian agricultural practice; and
- Australian MRLs in the Australia New Zealand Food Standards Code.[5]

A list of possible analytes spiked into this PT study's samples is presented in Table 1.

Table 1 List of Possible Analytes

| | | | |
|---|---|---|---|
| Abamectin | Cyhalothrin | Fipronil | Mevinphos |
| Acephate | Cypermethrin | Fludioxonil | Omethoate |
| Acetamiprid | Cyprodinil | Fluopyram | Oxamyl |
| Azinphos-methyl | 2,4-D | Glyphosate | Permethrin |
| Azoxystrobin | Deltamethrin | Hexachlorobenzene | Pirimicarb |
| Bifenazate | Diazinon | Imazalil | Prochloraz |
| Bifenthrin | Dicofol | Imidacloprid | Procymidone |
| Buprofezin | Dieldrin | Indoxacarb | Profenofos |
| Carbaryl | Difenoconazole | Iprodione | Propamocarb |
| Carbendazim | Dimethoate | Linuron | Propargite |
| Chlorfenvinphos | Endosulfan Sulfate | Maldison | Pyraclostrobin |
| Chlorothalonil | Fenamiphos | Maleic hydrazide | Spinosad |
| Chlorpyrifos | Fenhexamid | Metalaxyl | Spirotetramat |
| Chlorthal-dimethyl | Fenitrothion | Methamidophos | Thiabendazole |
| Clothianidin | Fenthion | Methidathion | Triadimefon |
| Cyfluthrin | Fenvalerate | Methomyl | Trifloxystrobin |

## 2.4 Test Material Preparation

Three test samples were prepared by adding pesticide standard solutions to pureed tomatoes (Sample S1), plums (Sample S2) and garlic (Sample S3).

The spiked values for the samples and corresponding Australian maximum residue limits (MRLs) from the Australia New Zealand Food Standards Code,[5] are presented in Table 2.

Table 2 Spiked Values of Test Samples

| Sample | Analyte | Spiked Value (mg/kg) | Uncertainty[a] (mg/kg) | MRL[b] (mg/kg) |
|---|---|---|---|---|
| S1 (Tomato) | Azoxystrobin | 0.600 | 0.030 | T1 |
| | Chlorpyrifos | 0.829 | 0.041 | T0.5 |
| | Difenoconazole | 1.01 | 0.05 | 1 |
| | Endosulfan sulfate | 0.400 | 0.020 | - |
| | Fenhexamid | 0.402 | 0.020 | T2 |
| S2 (Plum) | Acephate | 0.0495 | 0.0025 | - |
| | Deltamethrin | 0.0500 | 0.0025 | 0.05 |
| | Difenoconazole | 3.00 | 0.15 | 2.5 |
| | Endosulfan sulfate | 0.400 | 0.020 | - |
| | Imidacloprid | 0.251 | 0.013 | 0.5[c] |
| | Oxamyl | 0.0707 | 0.0035 | 0.05[d] |
| S3 (Garlic) | Cyprodinil | 1.49 | 0.07 | 3 |
| | Endosulfan sulfate | 0.400 | 0.020 | - |
| | Maleic hydrazide | 16.0 | 0.8 | 15[e] |
| | Spirotetramat | 0.250 | 0.012 | 0.5[f] |

[a] Estimated expanded uncertainty at 95% confidence interval using a coverage factor of 2.

[b] '*' indicates that the MRL is set at the limit of determination; 'T' indicates that the MRL is a temporary maximum residue limit.[5] In some cases, MRLs are for the sum of several different permitted residues.

[c] Sum of imidacloprid and metabolites containing the 6-chloropyridinylmethylene moiety, expressed as imidacloprid.

[d] Sum of oxamyl and 2-hydroxyimino-N,N-dimethyl-2-(methylthio)-acetamide, expressed as oxamyl.

[e] Sum of free and conjugated maleic hydrazide, expressed as maleic hydrazide.

[f] Sum of spirotetramat, and cis-3-(2,5-dimethylphenyl)-4-hydroxy-8-methoxy-1-azaspiro[4.5]dec-3-en-2-one, expressed as spirotetramat.

Additional sample preparation details are provided in Appendix 1.

## 2.5 Homogeneity and Stability of Test Materials

The process used to prepare, store and dispatch the test samples has been demonstrated to produce sufficiently homogeneous and stable samples for previous NMI PT studies of similar analytes and matrices. The results returned by participants also gave no reason to question the homogeneity or stability of the study's samples.

Reports in the Joint FAO/WHO Meeting on Pesticide Residues (JMPR) database,[6] together with results of previous NMI PT studies of similar analytes and matrices, gave some assurance that various pesticides would be stable in frozen produce. To assess possible instability, the results returned by participants were compared to the spiked values. For scored analytes, assigned values were between 81% and 107% of the spiked values. These values are

similar to values observed in previous studies, and give good support for the stability of the samples.

Additionally, homogeneity and stability testing was conducted for Samples S2 and S3. Samples were demonstrated to be sufficiently homogeneous and stable for the purposes of this PT study.

Further details on the homogeneity and stability assessment of this PT study's samples are given in Appendix 2.

### 2.6 Sample Storage, Dispatch and Receipt

After preparation, the samples were stored in a freezer at approximately -20 °C. Participants were sent 100 g portions of both spiked and unspiked Samples S1 and S2, and 50 g portions of both spiked and unspiked Sample S3. The samples were packaged into insulated polystyrene foam boxes with cooler bricks and dispatched by courier on 29 April 2024.

The following items were also sent to participants:

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

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

### 2.7 Instructions to Participants

Participants were instructed as follows:

- Quantitatively analyse the samples using your routine test method.
- The unspiked material need not be analysed, it is provided for participants to use if they wish.
- Participants need not test for all analytes listed.
- Please analyse the samples immediately after thawing and mixing thoroughly.
- For each analyte in each sample report a single result on as received basis in units of mg/kg 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 measurement uncertainty (e.g. $0.50 \pm 0.02$ mg/kg), if determined.
- Report any listed pesticide not tested as NT.
- Do not correct results for any pesticide found in the unspiked sample.
- 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.
- Give details of your methodology and basis of uncertainty estimate 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 27 May 2024 by email to proficiency@measurement.gov.au.

The results due date was later extended to 11 June 2024 due to sample delivery delays to some international participants.

### 2.8 Interim Report and Preliminary Report

An Interim Report was emailed to all participants on 13 June 2024.

A Preliminary Report was emailed to all participants on 21 June 2024. 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. In the Preliminary Report, assigned values were not set for Sample S2 acephate, deltamethrin, endosulfan sulfate and imidacloprid as it was intended for these analytes to have reference values by isotope dilution mass spectrometry (IDMS). These analytes have now been set assigned values as reference values by IDMS for this Final Report, and participants' results for these analytes have now been scored.

## 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 4.

### 3.2 Basis of Participants' Measurement Uncertainty Estimates

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

Table 3 Basis of MU 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<br>k = 2 | Duplicate analysis<br>Instrument calibration | CRM<br>Instrument calibration<br>Recoveries of SS | ISO/GUM |
| 2 | Top Down - precision and estimates of the method and laboratory bias<br>k = 2 | Duplicate analysis<br>Instrument calibration | Instrument calibration<br>Recoveries of SS<br>Standard purity | Codex CAC/GL 59-2006 "Guidelines on Estimation of Uncertainty of Results" Annex 5.4 |
| 3 | Top Down - precision and estimates of the method and laboratory bias<br>Coverage factor not reported | Duplicate analysis<br>Instrument calibration | Instrument calibration<br>Laboratory bias from PT studies<br>Recoveries of SS<br>Standard purity | |
| 4 | Horwitz formula<br>Coverage factor not reported | Control samples - SS<br>Duplicate analysis | CRM<br>Recoveries of SS | NMI Uncertainty Course |
| 5 | Top Down - precision and estimates of the method and laboratory bias<br>Coverage factor not reported | Control samples | CRM<br>Recoveries of SS<br>Standard purity | ISO/GUM |
| 6 | Top Down - precision and estimates of the method and laboratory bias<br>k = 2 | Duplicate analysis | Recoveries of SS | NMI Uncertainty Course |
| 7 | Top Down - reproducibility (standard deviation) from PT studies used directly<br>Coverage factor not reported | Standard deviation from PT studies only | | SANTE 12682/2019 |
| 8 | Top Down - precision and estimates of the method and laboratory bias<br>k = 2 | Duplicate analysis | Recoveries of SS<br>Standard purity | Eurachem/CITAC Guide |

| Lab. Code | Approach to Estimating MU | Information Sources for MU Estimation* | | Guide Document for Estimating MU |
|---|---|---|---|---|
| | | Precision | Method Bias | |
| 9 | Top Down - precision and estimates of the method and laboratory bias<br>k = 2 | Control samples<br>Duplicate analysis<br>Instrument calibration | CRM<br>Recoveries of SS<br>Standard purity | SANTE 12682/2019 |
| 10 | Top Down - precision and estimates of the method and laboratory bias<br>Coverage factor not reported | Control samples - SS | Recoveries of SS | NATA Technical Note 33 |
| 11 | Standard deviation of replicate analyses multiplied by 2 or 3<br>k = 2 | Duplicate analysis<br>Instrument calibration | Instrument calibration<br>Recoveries of SS<br>Standard purity | Eurachem/CITAC Guide |
| 12 | Top Down - precision and estimates of the method and laboratory bias<br>Coverage factor not reported | Control samples - CRM<br>Duplicate analysis<br>Instrument calibration | CRM<br>Instrument calibration<br>Recoveries of SS<br>Standard purity | Eurolab Technical Report 1/2007 |
| 13 | Top Down - precision and estimates of the method and laboratory bias<br>k = 2 | Duplicate analysis<br>Instrument calibration | Instrument calibration<br>Recoveries of SS<br>Standard purity | |
| 14 | Coverage factor not reported | Duplicate analysis<br>Instrument calibration | Recoveries of SS | |
| 15 | Top Down - precision and estimates of the method and laboratory bias<br>k = 2 | Control samples - SS | Recoveries of SS<br>Standard purity | SANTE 12682/2019 |
| 16 | Top Down - precision and estimates of the method and laboratory bias<br>Coverage factor not reported | Control samples - SS<br>Duplicate analysis | Standard purity | Eurachem/CITAC Guide |

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

### 3.3 Participants' Comments

Participants were invited to make any comments on the samples, this study, or possible future studies. Such feedback may be useful in improving future studies. Participants' comments, and the study coordinator's response (if applicable) are presented in Table 4. Some responses may be modified so that the participant cannot be identified.

Table 4 Participants' Comments

| Lab. Code | Sample | Participant's Comments | Study Coordinator's Response |
|---|---|---|---|
| 1 | S2 | 2,4-D detected in blank and sample at ~0.007mg/kg | |
| 2 | S1 | Chlorpyrifos methodology: GC NPD for qualitative analysis<br>Difenoconazole and endosulfan sulfate methodology: GC MS for qualitative analysis | |
| | S2 | Deltamethrin methodology: GC-ECD for qualitative analysis<br>Difenoconazole and endosulfan sulfate methodology: GC MS for qualitative analysis | |
| | S3 | Endosulfan sulfate methodology: GC MS for qualitative analysis | |
| 4 | S2 | Acephate value is factored for recovery. | |
| 8 | All | Please include sample preparation procedure to each kind of sample/matrix so we can replicate in case when we lack sample for analysis. | We can provide this information on request.<br>The sample preparation for previous studies can also be found in our Final Reports. |
| 10 | S3 | The result for Maleic Hydrazide has been recovery corrected. | |
| 15 | S1 | Chlorpyrifos and endosulfan sulfate methodology: Confirmatory analysis using GC-MS | |
| | S2 | Endosulfan sulfate methodology: Confirmatory analysis using GC-MS | |
| | S3 | Endosulfan sulfate methodology: Confirmatory analysis using GC-MS | |
| | All | The concentration of residue reported is an average of four determinations made on the same sample. The unspiked sample was also analysed and found to have no residues at or above the Limit of Quantitation (LOQ) at 0.01 mg/Kg.<br>This PT is important for the reliability and assessment of our laboratory's results, and also for compliance in accreditation. We would like to suggests PT studies for pesticide residues in other sample matrices such as rice, banana, pineapple, and mango.<br>Uncertainty: The reported uncertainty of result is an expanded uncertainty calculated using a coverage factor of 2 which gives a level of confidence of approximately 95%. | Thank you for your feedback, we will take into consideration your suggestions for matrices when planning future studies. |
| 16 | S3 | Maleic hydrazide methodology: Glyphosate/maleic<br>Blank Garlic contain Maleic Hydrazide 1.05 mg/kg --(LOR <1 mg/kg) | |

# 4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

## 4.1 Results Summary

Participant results are listed in Tables 5 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), and other estimates of analyte mass fraction. Bar charts of results and performance scores are presented in Figures 2 to 16. An example chart with interpretation guide is shown in Figure 1.

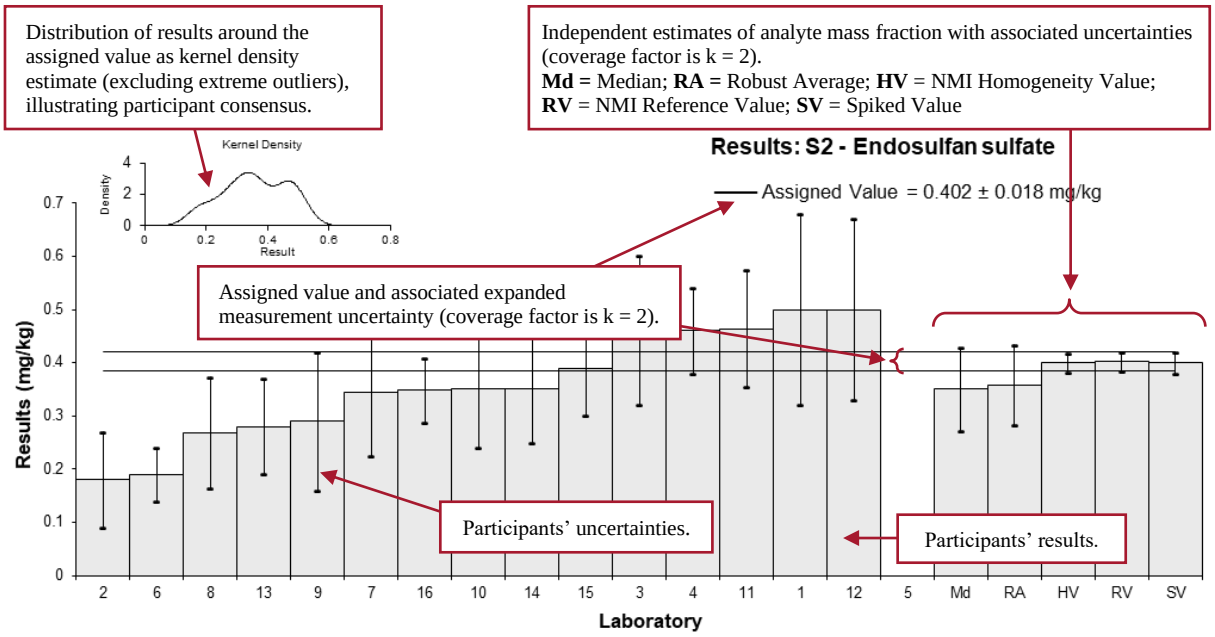



Figure 1 Guide to Presentation of Results

## 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 (when using the robust average).[3,4] Extreme outliers were obvious blunders, e.g. results reported with incorrect units or for a different analyte, and such results were removed for the calculation of all statistics.[3,4]

The results reported by Laboratory **13** in Sample S1 were all lower than the robust average of participants' results by approximately the same factor (0.6), which is an indication of laboratory bias. To avoid bias in calculation of the assigned value and unfair scoring, these results were excluded from robust average calculations; 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 testing item'.[1] In this PT study, this property is the mass fraction of the analytes in the samples. The assigned values for Sample S2 acephate, deltamethrin, endosulfan sulfate and imidacloprid were reference values as determined by IDMS. The assigned values for all other scored analytes were the robust averages of participants' results, and the expanded uncertainties were estimated from the associated robust SDs (Appendix 3).

## 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 using the procedure described in ISO 13528.[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 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 when the PCV remains the same.

### 4.6 Target Standard Deviation for Proficiency Assessment

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

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

### 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 for proficiency assessment 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.

### 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 expanded 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:

- $|E_n| < 1.0$ 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 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** | Tomato |
| **Analyte** | Azoxystrobin |
| **Unit** | mg/kg |

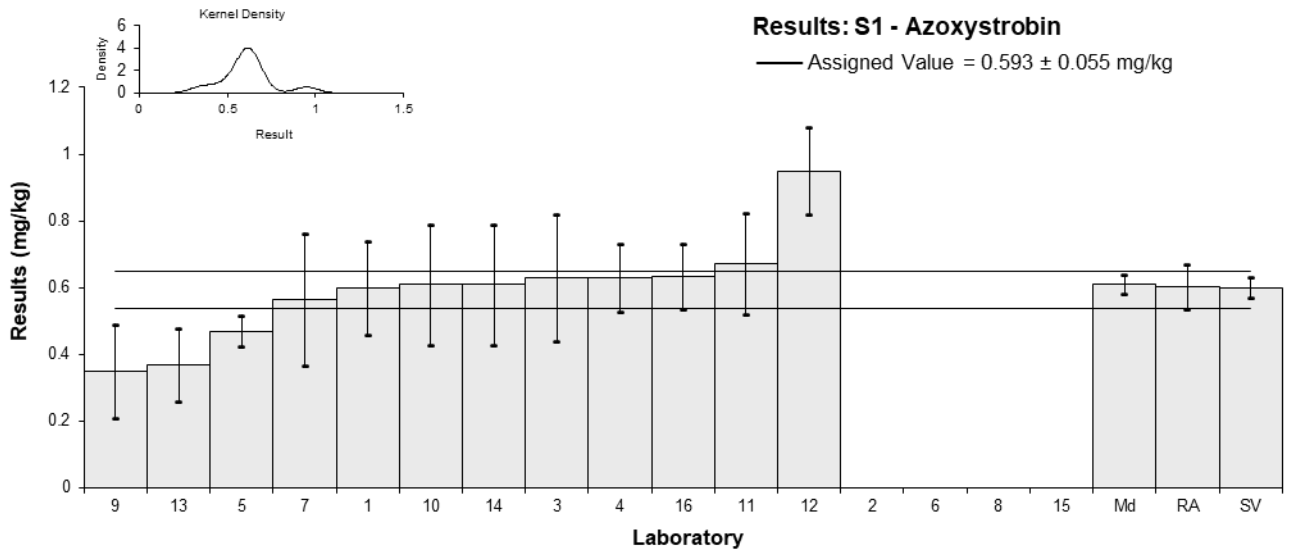
**Participant Results**

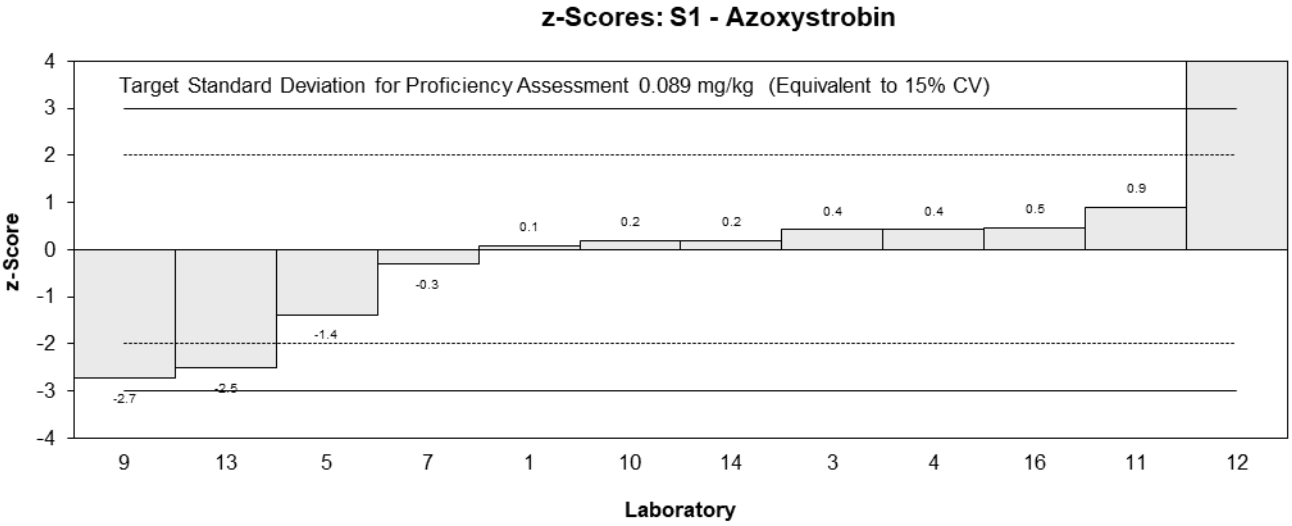
| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.60 | 0.14 | 99 | 0.08 | 0.05 |
| **2** | NT | NT | NT | | |
| **3** | 0.63 | 0.19 | 80 | 0.42 | 0.19 |
| **4** | 0.63 | 0.1 | 108 | 0.42 | 0.32 |
| **5** | 0.47 | 0.047 | 96.12 | -1.38 | -1.70 |
| **6** | NT | NT | NT | | |
| **7** | 0.565 | 0.198 | 79 | -0.31 | -0.14 |
| **8** | NT | NT | NT | | |
| **9** | 0.35 | 0.14 | 109 | -2.73 | -1.62 |
| **10** | 0.61 | 0.18 | 101 | 0.19 | 0.09 |
| **11** | 0.672 | 0.15 | 92 | 0.89 | 0.49 |
| **12*** | 0.95 | 0.13 | 87 | 4.01 | 2.53 |
| **13**** | 0.37 | 0.11 | 121 | -2.51 | -1.81 |
| **14** | 0.61 | 0.18 | 85 | 0.19 | 0.09 |
| **15** | NT | NT | NT | | |
| **16** | 0.635 | 0.098 | 110.9 | 0.47 | 0.37 |

* Outlier, ** Excluded Result, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.593 | 0.055 |
| **Spike Value** | 0.600 | 0.030 |
| **Robust Average** | 0.602 | 0.068 |
| **Median** | 0.610 | 0.028 |
| **Mean** | 0.611 | |
| **N** | 11 | |
| **Max** | 0.95 | |
| **Min** | 0.35 | |
| **Robust SD** | 0.090 | |
| **Robust CV** | 15% | |


Kernel Density
Density
Result
Results: S1 - Azoxystrobin
Assigned Value = 0.593 ± 0.055 mg/kg
Results (mg/kg)
Laboratory
9 13 5 7 1 10 14 3 4 16 11 12 2 6 8 15 Md RA SV


z-Scores: S1 - Azoxystrobin
Target Standard Deviation for Proficiency Assessment 0.089 mg/kg (Equivalent to 15% CV)
z-Score
-2.7 -2.5 -1.4 -0.3 0.1 0.2 0.2 0.4 0.4 0.5 0.9
Laboratory
9 13 5 7 1 10 14 3 4 16 11 12

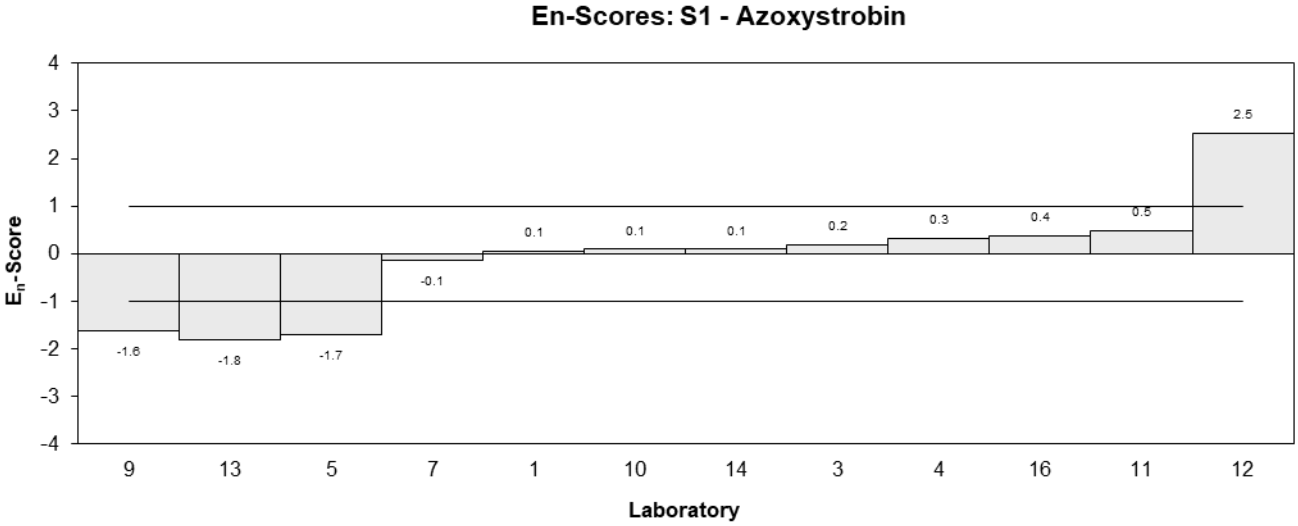

En-Scores: S1 - Azoxystrobin
En-Score
-1.6 -1.8 -1.7 -0.1 0.1 0.1 0.1 0.2 0.3 0.4 0.5 2.5
Laboratory
9 13 5 7 1 10 14 3 4 16 11 12

Figure 2

Table 6

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Tomato |
| **Analyte** | Chlorpyrifos |
| **Unit** | mg/kg |

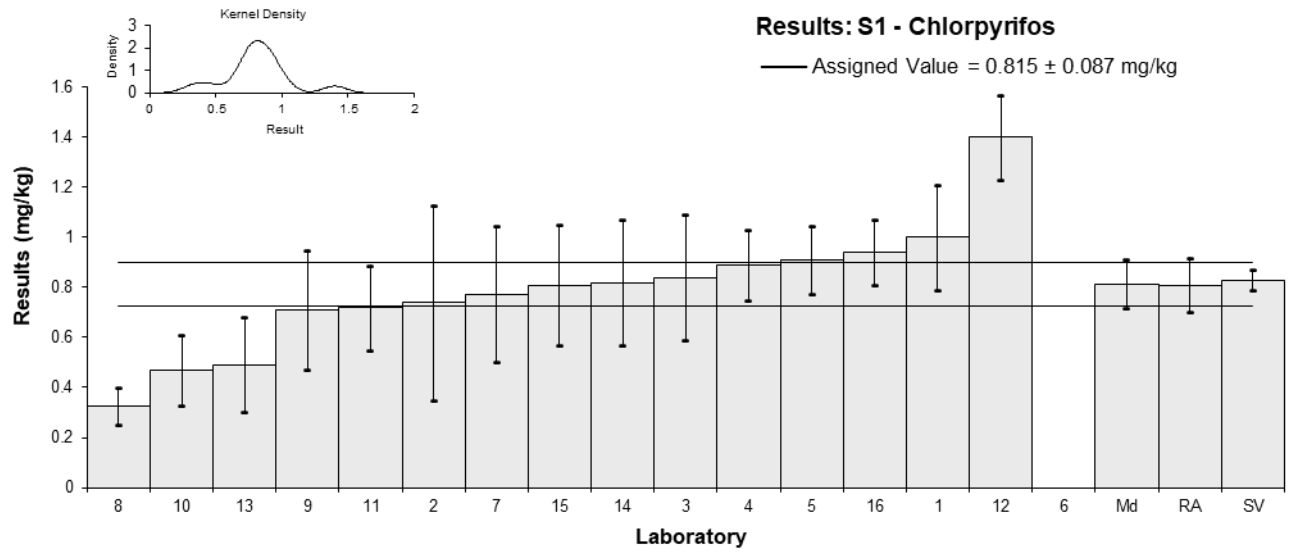
**Participant Results**

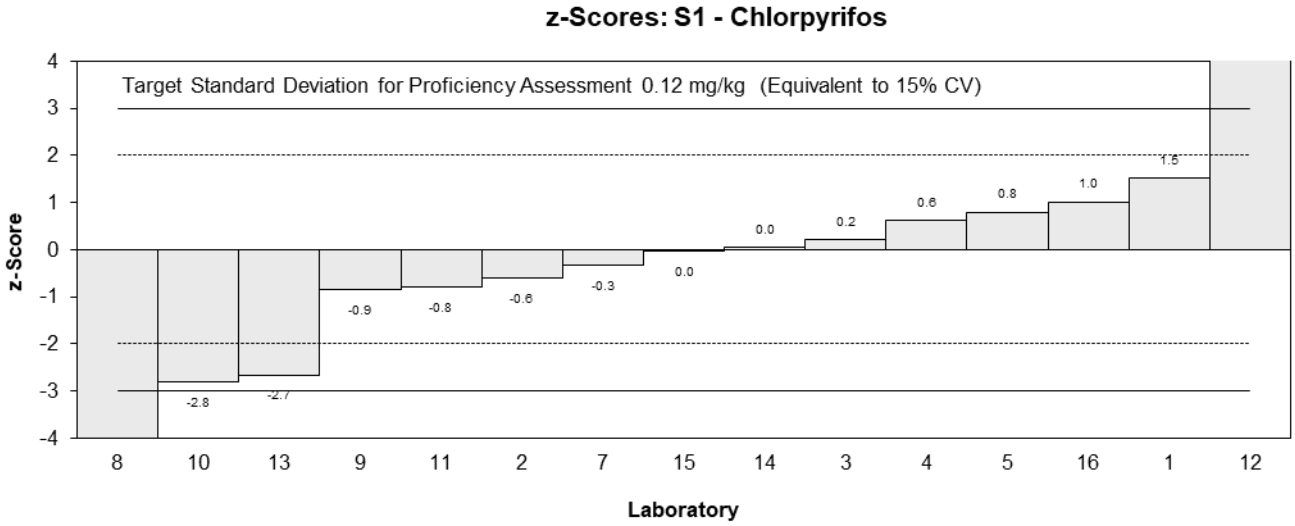
| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 1.0 | 0.21 | 78 | 1.51 | 0.81 |
| **2** | 0.74 | 0.39 | 77 | -0.61 | -0.19 |
| **3** | 0.84 | 0.25 | 108 | 0.20 | 0.09 |
| **4** | 0.89 | 0.14 | 99 | 0.61 | 0.46 |
| **5** | 0.91 | 0.1365 | 89.56 | 0.78 | 0.59 |
| **6** | >0.1 | NR | NR | | |
| **7** | 0.774 | 0.271 | 79 | -0.34 | -0.14 |
| **8*** | 0.325 | 0.074 | 43 | -4.01 | -4.29 |
| **9** | 0.71 | 0.24 | 114 | -0.86 | -0.41 |
| **10** | 0.47 | 0.14 | 93 | -2.82 | -2.09 |
| **11** | 0.719 | 0.17 | 107 | -0.79 | -0.50 |
| **12*** | 1.4 | 0.17 | 90 | 4.79 | 3.06 |
| **13**** | 0.49 | 0.19 | 89 | -2.66 | -1.56 |
| **14** | 0.82 | 0.25 | 92 | 0.04 | 0.02 |
| **15** | 0.81 | 0.24 | 103 | -0.04 | -0.02 |
| **16** | 0.939 | 0.13 | 83 | 1.01 | 0.79 |

* Outlier, ** Excluded Result, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.815 | 0.087 |
| **Spike Value** | 0.829 | 0.041 |
| **Robust Average** | 0.81 | 0.11 |
| **Median** | 0.815 | 0.095 |
| **Mean** | 0.81 | |
| **N** | 14 | |
| **Max** | 1.4 | |
| **Min** | 0.325 | |
| **Robust SD** | 0.17 | |
| **Robust CV** | 21% | |


Kernel Density
Density
Result
Results: S1 - Chlorpyrifos
Assigned Value = 0.815 ± 0.087 mg/kg
Results (mg/kg)
Laboratory
8 10 13 9 11 2 7 15 14 3 4 5 16 1 12 6 Md RA SV


z-Scores: S1 - Chlorpyrifos
Target Standard Deviation for Proficiency Assessment 0.12 mg/kg (Equivalent to 15% CV)
z-Score
-2.8 -2.7 -0.9 -0.8 -0.6 -0.3 0.0 0.0 0.2 0.6 0.8 1.0 1.5
Laboratory
8 10 13 9 11 2 7 15 14 3 4 5 16 1 12

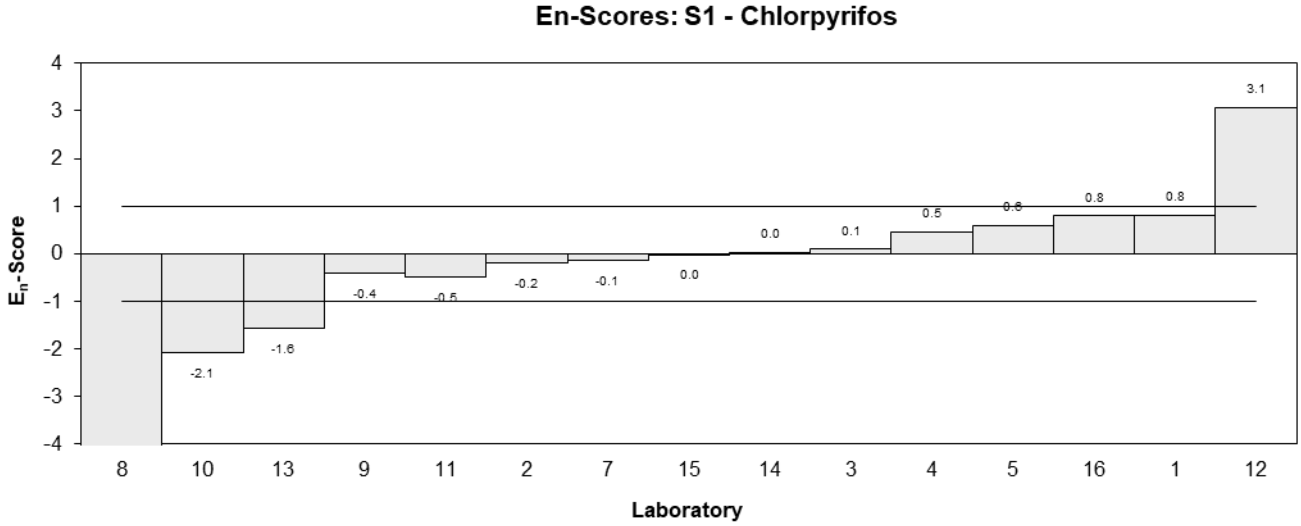

En-Scores: S1 - Chlorpyrifos
En-Score
-2.1 -1.6 -0.4 -0.5 -0.2 -0.1 0.0 0.0 0.1 0.5 0.6 0.8 0.8 3.1
Laboratory
8 10 13 9 11 2 7 15 14 3 4 5 16 1 12

Figure 3

Table 7

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Tomato |
| **Analyte** | Difenoconazole |
| **Unit** | mg/kg |

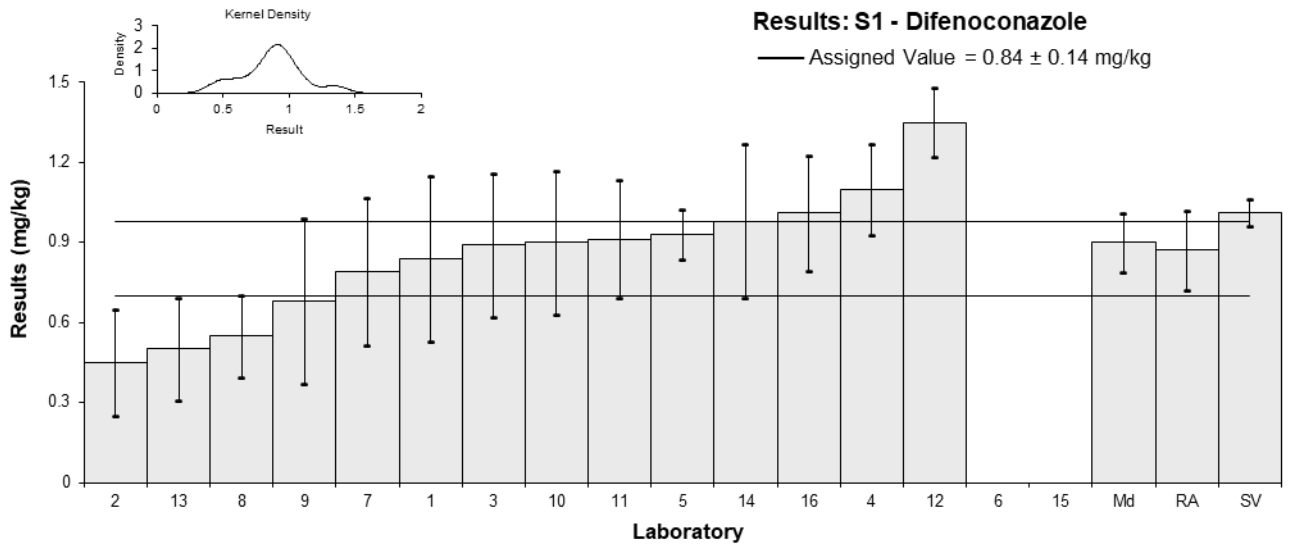
**Participant Results**

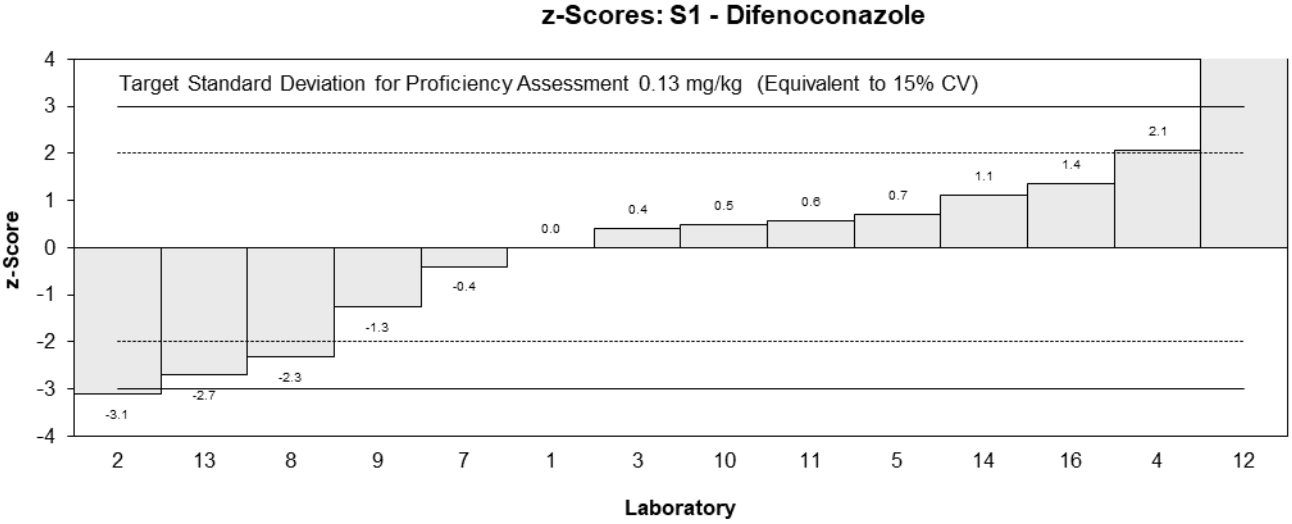
| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.84 | 0.31 | 87 | 0.00 | 0.00 |
| **2** | 0.45 | 0.20 | 98 | -3.10 | -1.60 |
| **3** | 0.89 | 0.27 | 81 | 0.40 | 0.16 |
| **4** | 1.1 | 0.17 | 88 | 2.06 | 1.18 |
| **5** | 0.93 | 0.093 | 93.14 | 0.71 | 0.54 |
| **6** | NT | NT | NT | | |
| **7** | 0.790 | 0.277 | 84 | -0.40 | -0.16 |
| **8** | 0.548 | 0.154 | 55 | -2.32 | -1.40 |
| **9** | 0.68 | 0.31 | 81 | -1.27 | -0.47 |
| **10** | 0.90 | 0.27 | 105 | 0.48 | 0.20 |
| **11** | 0.913 | 0.22 | 88 | 0.58 | 0.28 |
| **12*** | 1.35 | 0.13 | 83 | 4.05 | 2.67 |
| **13**** | 0.50 | 0.19 | 95 | -2.70 | -1.44 |
| **14** | 0.98 | 0.29 | 86 | 1.11 | 0.43 |
| **15** | NT | NT | NT | | |
| **16** | 1.01 | 0.215 | 97 | 1.35 | 0.66 |

* Outlier, ** Excluded Result, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.84 | 0.14 |
| **Spike Value** | 1.01 | 0.05 |
| **Robust Average** | 0.87 | 0.15 |
| **Median** | 0.90 | 0.11 |
| **Mean** | 0.88 | |
| **N** | 13 | |
| **Max** | 1.35 | |
| **Min** | 0.45 | |
| **Robust SD** | 0.22 | |
| **Robust CV** | 25% | |


Kernel Density
Density
Result
Results: S1 - Difenoconazole
Assigned Value = 0.84 ± 0.14 mg/kg
Results (mg/kg)
Laboratory
2 13 8 9 7 1 3 10 11 5 14 16 4 12 6 15 Md RA SV


z-Scores: S1 - Difenoconazole
Target Standard Deviation for Proficiency Assessment 0.13 mg/kg (Equivalent to 15% CV)
z-Score
-3.1 -2.7 -2.3 -1.3 -0.4 0.0 0.4 0.5 0.6 0.7 1.1 1.4 2.1
Laboratory
2 13 8 9 7 1 3 10 11 5 14 16 4 12

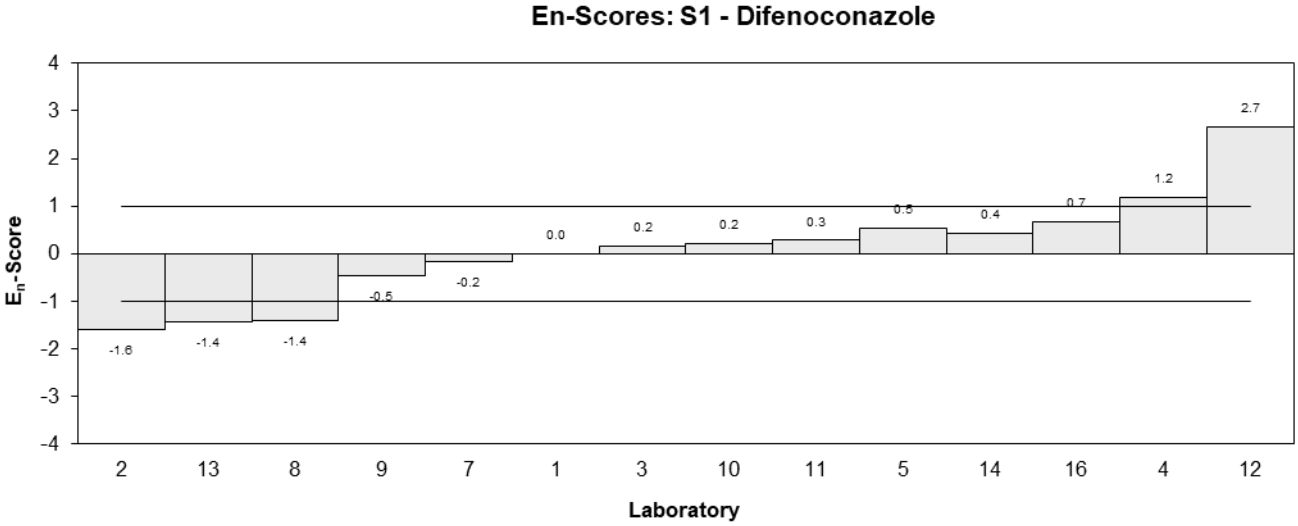

En-Scores: S1 - Difenoconazole
En-Score
-1.6 -1.4 -1.4 -0.5 -0.2 0.0 0.2 0.2 0.3 0.5 0.4 0.7 1.2 2.7
Laboratory
2 13 8 9 7 1 3 10 11 5 14 16 4 12

Figure 4

Table 8

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Tomato |
| **Analyte** | Endosulfan sulfate |
| **Unit** | mg/kg |

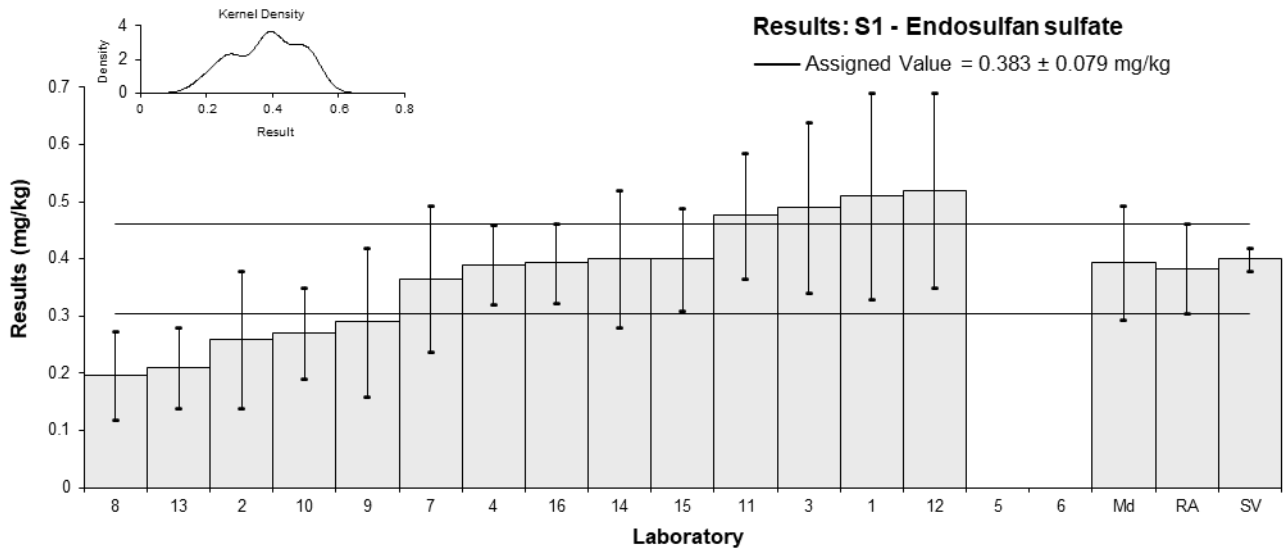
**Participant Results**

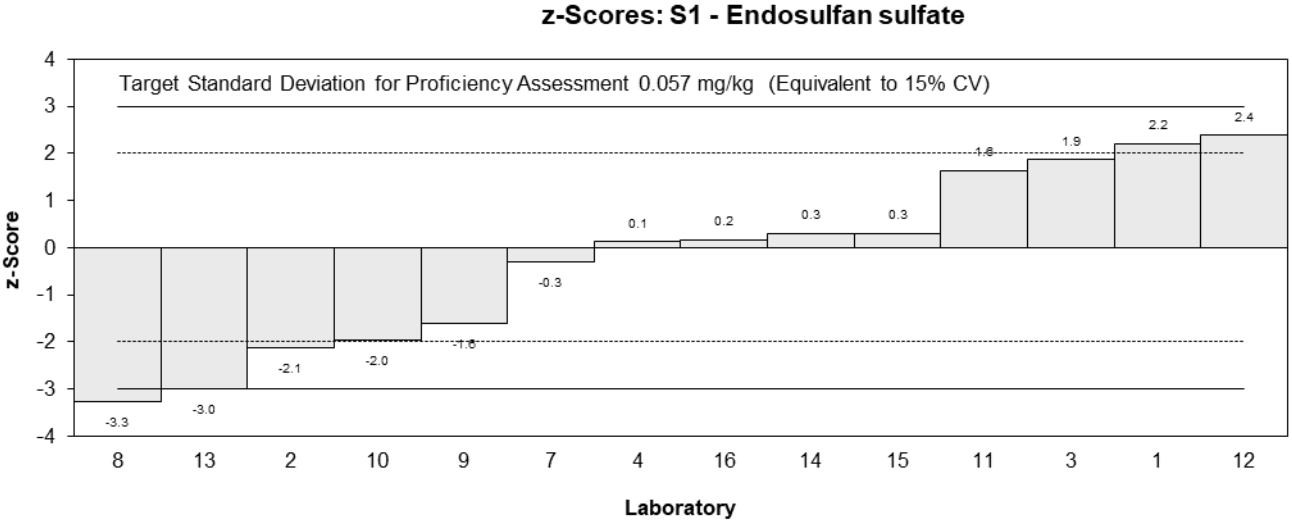
| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.51 | 0.18 | 102 | 2.21 | 0.65 |
| **2** | 0.26 | 0.12 | 83 | -2.14 | -0.86 |
| **3** | 0.49 | 0.15 | 89 | 1.86 | 0.63 |
| **4** | 0.39 | 0.07 | 101 | 0.12 | 0.07 |
| **5** | NT | NT | NT | | |
| **6** | NT | NT | NT | | |
| **7** | 0.365 | 0.128 | 86 | -0.31 | -0.12 |
| **8** | 0.196 | 0.077 | 74 | -3.26 | -1.70 |
| **9** | 0.29 | 0.13 | 105 | -1.62 | -0.61 |
| **10** | 0.27 | 0.08 | 98 | -1.97 | -1.01 |
| **11** | 0.476 | 0.11 | 91 | 1.62 | 0.69 |
| **12** | 0.52 | 0.17 | 52 | 2.38 | 0.73 |
| **13**** | 0.21 | 0.07 | 105 | -3.01 | -1.64 |
| **14** | 0.40 | 0.12 | 85 | 0.30 | 0.12 |
| **15** | 0.4 | 0.09 | 98 | 0.30 | 0.14 |
| **16** | 0.393 | 0.07 | 70 | 0.17 | 0.09 |

** Excluded Result, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.383 | 0.079 |
| **Spike Value** | 0.400 | 0.020 |
| **Robust Average** | 0.383 | 0.079 |
| **Median** | 0.393 | 0.100 |
| **Mean** | 0.382 | |
| **N** | 13 | |
| **Max** | 0.52 | |
| **Min** | 0.196 | |
| **Robust SD** | 0.11 | |
| **Robust CV** | 30% | |


Kernel Density
Density
Result
Results: S1 - Endosulfan sulfate
Assigned Value = 0.383 ± 0.079 mg/kg
Results (mg/kg)
Laboratory
8 13 2 10 9 7 4 16 14 15 11 3 1 12 5 6 Md RA SV


z-Scores: S1 - Endosulfan sulfate
Target Standard Deviation for Proficiency Assessment 0.057 mg/kg (Equivalent to 15% CV)
z-Score
-3.3 -3.0 -2.1 -2.0 -1.6 -0.3 0.1 0.2 0.3 0.3 1.6 1.9 2.2 2.4
Laboratory
8 13 2 10 9 7 4 16 14 15 11 3 1 12

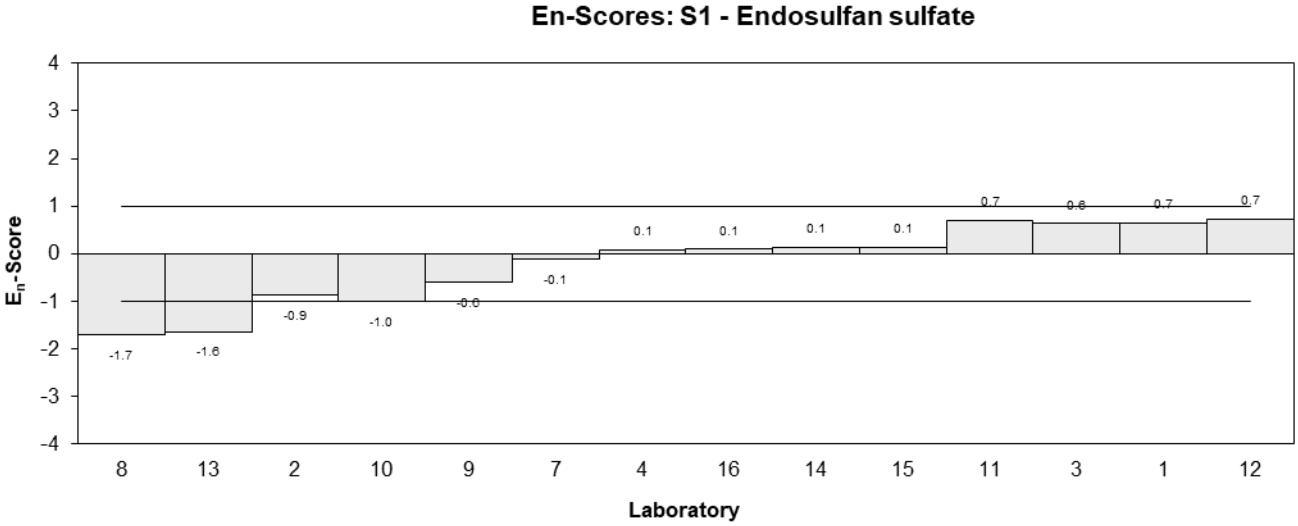

En-Scores: S1 - Endosulfan sulfate
En-Score
-1.7 -1.6 -0.9 -1.0 -0.6 -0.1 0.1 0.1 0.1 0.1 0.7 0.6 0.7 0.7
Laboratory
8 13 2 10 9 7 4 16 14 15 11 3 1 12

Figure 5

Table 9

**Sample Details**

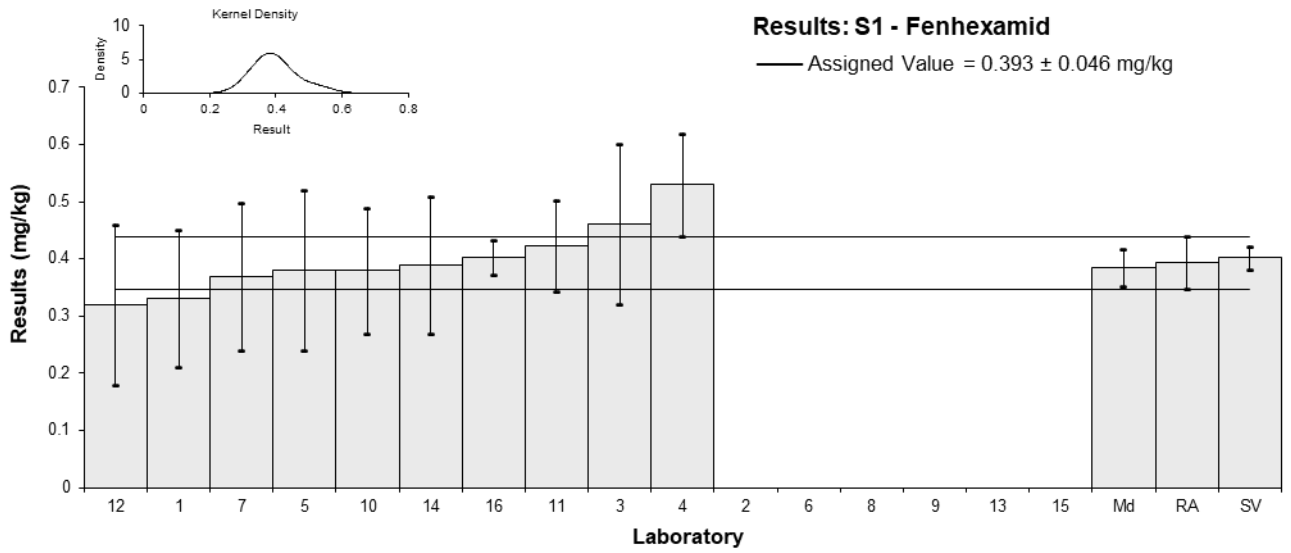
| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Tomato |
| **Analyte** | Fenhexamid |
| **Unit** | mg/kg |

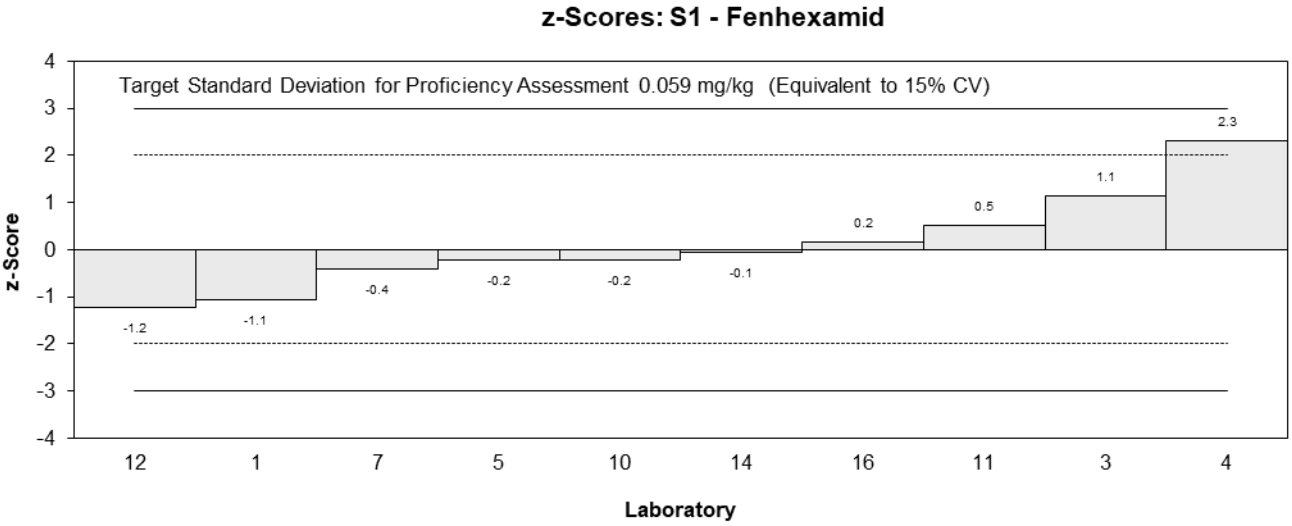
**Participant Results**

| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.33 | 0.12 | 100 | -1.07 | -0.49 |
| **2** | NT | NT | NT | | |
| **3** | 0.46 | 0.14 | 59 | 1.14 | 0.45 |
| **4** | 0.53 | 0.09 | 106 | 2.32 | 1.36 |
| **5** | 0.38 | 0.1395 | 90 | -0.22 | -0.09 |
| **6** | NT | NT | NT | | |
| **7** | 0.369 | 0.129 | 81 | -0.41 | -0.18 |
| **8** | NT | NT | NT | | |
| **9** | NT | NT | NT | | |
| **10** | 0.38 | 0.11 | 110 | -0.22 | -0.11 |
| **11** | 0.423 | 0.08 | 92 | 0.51 | 0.33 |
| **12** | 0.32 | 0.14 | 70 | -1.24 | -0.50 |
| **13** | NT | NT | NT | | |
| **14** | 0.39 | 0.12 | 106 | -0.05 | -0.02 |
| **15** | NT | NT | NT | | |
| **16** | 0.402 | 0.03 | 105.1 | 0.15 | 0.16 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.393 | 0.046 |
| **Spike Value** | 0.402 | 0.020 |
| **Robust Average** | 0.393 | 0.046 |
| **Median** | 0.385 | 0.032 |
| **Mean** | 0.398 | |
| **N** | 10 | |
| **Max** | 0.53 | |
| **Min** | 0.32 | |
| **Robust SD** | 0.058 | |
| **Robust CV** | 15% | |


Kernel Density
Density
Result
Results: S1 - Fenhexamid
Assigned Value = 0.393 ± 0.046 mg/kg
Results (mg/kg)
Laboratory
12 1 7 5 10 14 16 11 3 4 2 6 8 9 13 15 Md RA SV


z-Scores: S1 - Fenhexamid
Target Standard Deviation for Proficiency Assessment 0.059 mg/kg (Equivalent to 15% CV)
z-Score
-1.2 -1.1 -0.4 -0.2 -0.2 -0.1 0.2 0.5 1.1 2.3
Laboratory
12 1 7 5 10 14 16 11 3 4

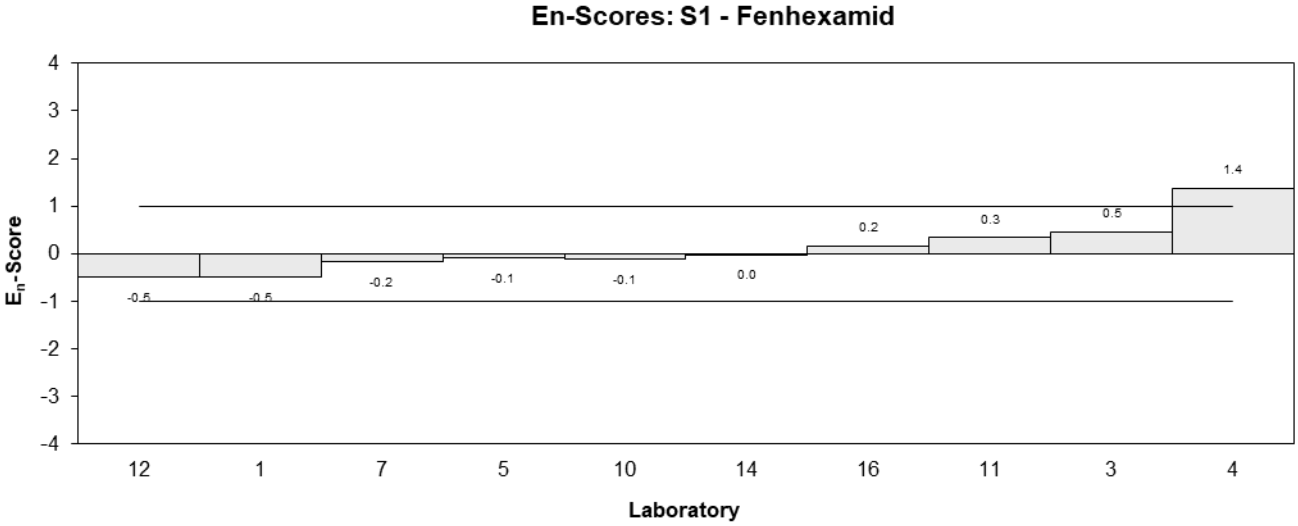

En-Scores: S1 - Fenhexamid
En-Score
-0.5 -0.5 -0.2 -0.1 -0.1 0.0 0.2 0.3 0.5 1.4
Laboratory
12 1 7 5 10 14 16 11 3 4

Figure 6

Table 10

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Plum |
| **Analyte** | Acephate |
| **Unit** | mg/kg |

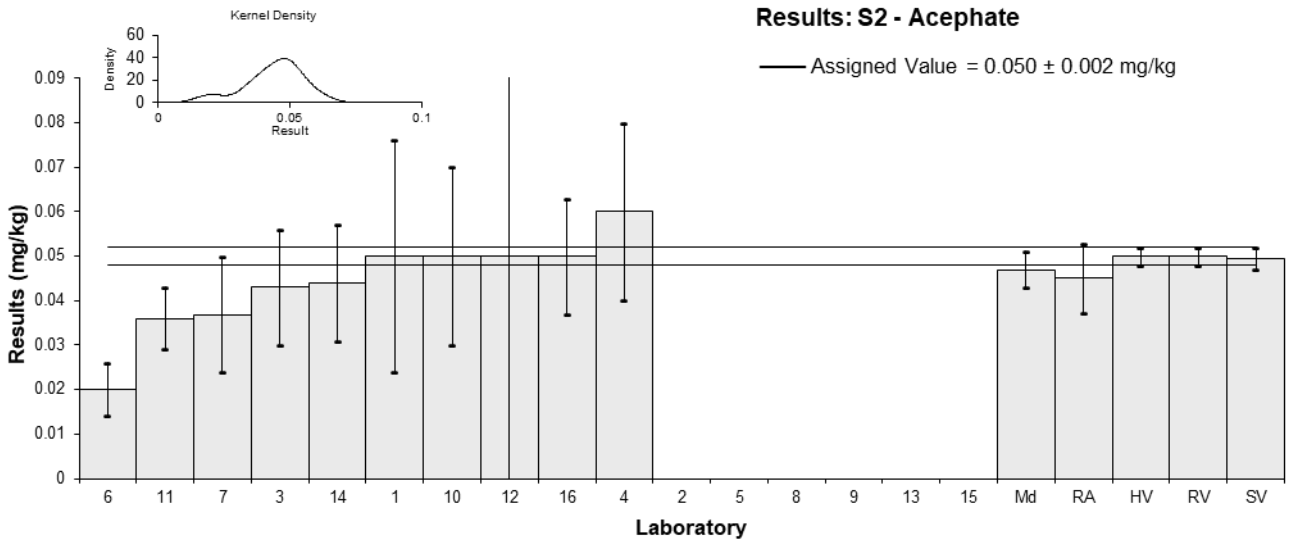
**Participant Results**

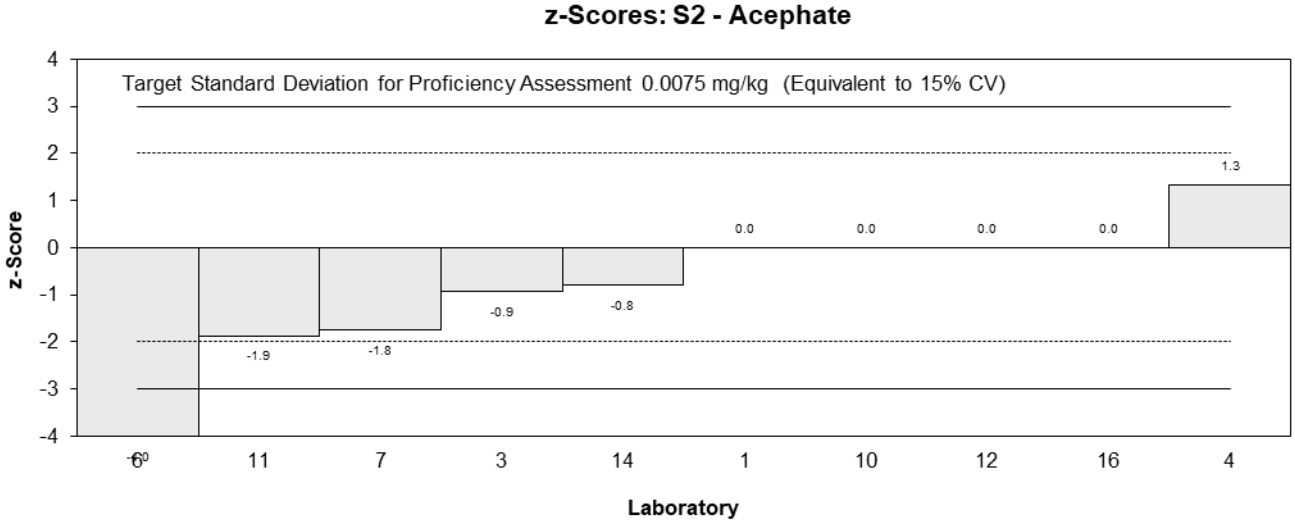
| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.05 | 0.026 | NR | 0.00 | 0.00 |
| **2** | NT | NT | NT | | |
| **3** | 0.043 | 0.013 | 65 | -0.93 | -0.53 |
| **4** | 0.06 | 0.02 | 75 | 1.33 | 0.50 |
| **5** | NT | NT | NT | | |
| **6** | 0.02 | 0.006 | NR | -4.00 | -4.74 |
| **7** | 0.0369 | 0.0129 | 85 | -1.75 | -1.00 |
| **8** | NT | NT | NT | | |
| **9** | NT | NT | NT | | |
| **10** | 0.05 | 0.02 | 102 | 0.00 | 0.00 |
| **11** | 0.036 | 0.007 | 70 | -1.87 | -1.92 |
| **12** | 0.05 | 0.13 | 82 | 0.00 | 0.00 |
| **13** | NT | NT | NT | | |
| **14** | 0.044 | 0.013 | 90 | -0.80 | -0.46 |
| **15** | NT | NT | NT | | |
| **16** | 0.05 | 0.013 | 78 | 0.00 | 0.00 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.050 | 0.002 |
| **Spike Value** | 0.0495 | 0.0025 |
| **Homogeneity Value** | 0.050 | 0.002 |
| **Reference Value** | 0.050 | 0.002 |
| **Robust Average** | 0.0450 | 0.0079 |
| **Median** | 0.0470 | 0.0041 |
| **Mean** | 0.0440 | |
| **N** | 10 | |
| **Max** | 0.06 | |
| **Min** | 0.02 | |
| **Robust SD** | 0.010 | |
| **Robust CV** | 22% | |

Assigned value is the reference value as determined by IDMS.


Results: S2 - Acephate
Assigned Value = 0.050 ± 0.002 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
6 11 7 3 14 1 10 12 16 4 2 5 8 9 13 15 Md RA HV RV SV


z-Scores: S2 - Acephate
Target Standard Deviation for Proficiency Assessment 0.0075 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
6 11 7 3 14 1 10 12 16 4
-1.9
-1.8
-0.9
-0.8
0.0
1.3

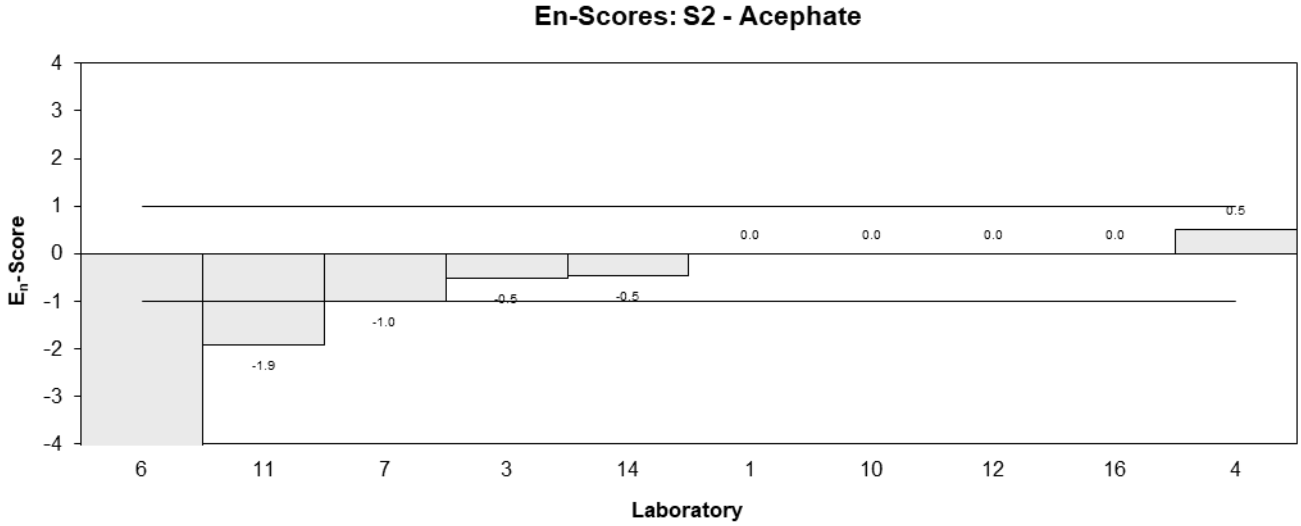

En-Scores: S2 - Acephate
En-Score
Laboratory
6 11 7 3 14 1 10 12 16 4
-1.9
-1.0
-0.5
-0.5
0.0
0.5

Figure 7

Table 11

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Plum |
| **Analyte** | Deltamethrin |
| **Unit** | mg/kg |

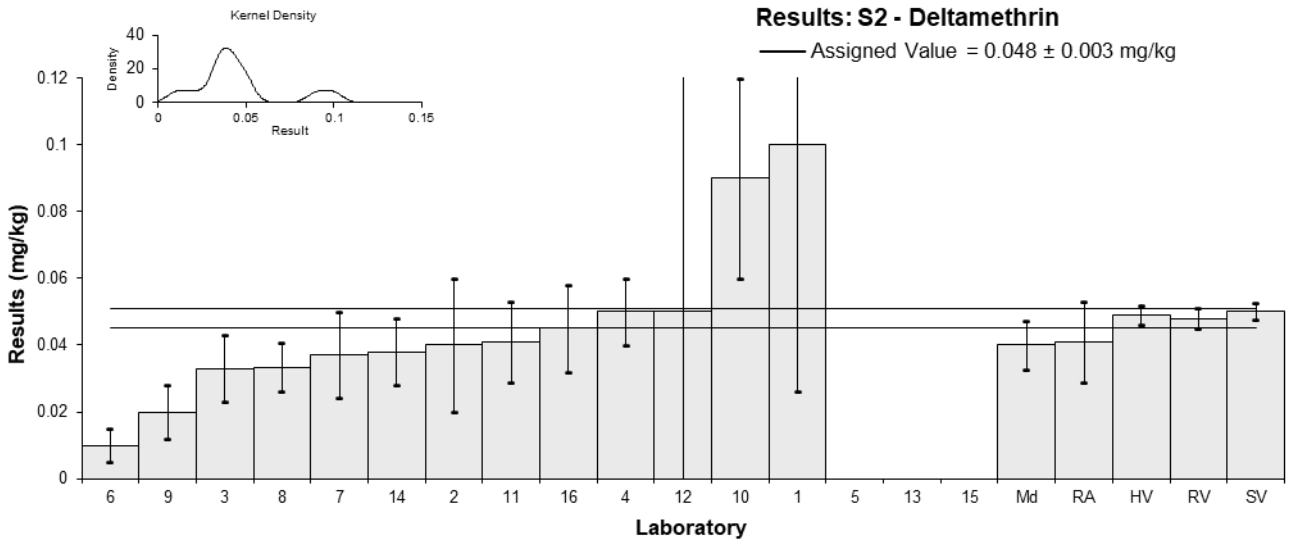
**Participant Results**

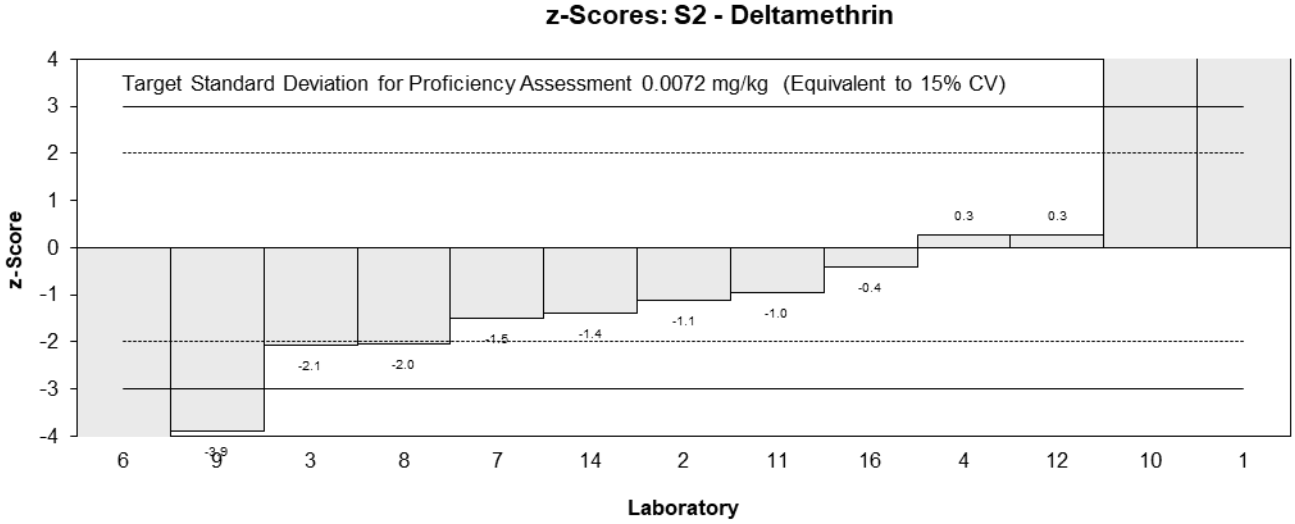
| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.10 | 0.074 | 107 | 7.22 | 0.70 |
| **2** | 0.04 | 0.02 | 93 | -1.11 | -0.40 |
| **3** | 0.033 | 0.010 | 110 | -2.08 | -1.44 |
| **4** | 0.05 | 0.01 | 97 | 0.28 | 0.19 |
| **5** | NT | NT | NT | | |
| **6** | 0.01 | 0.005 | NR | -5.28 | -6.52 |
| **7** | 0.0371 | 0.0130 | 95 | -1.51 | -0.82 |
| **8** | 0.0333 | 0.0073 | 88 | -2.04 | -1.86 |
| **9** | 0.02 | 0.008 | 63 | -3.89 | -3.28 |
| **10** | 0.09 | 0.03 | 79 | 5.83 | 1.39 |
| **11** | 0.041 | 0.012 | 80 | -0.97 | -0.57 |
| **12** | 0.05 | 0.16 | 86 | 0.28 | 0.01 |
| **13** | NR | NR | 105 | | |
| **14** | 0.038 | 0.01 | 71 | -1.39 | -0.96 |
| **15** | <0.01 | NR | NR | | |
| **16** | 0.045 | 0.013 | 96 | -0.42 | -0.22 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.048 | 0.003 |
| **Spike Value** | 0.0500 | 0.0025 |
| **Homogeneity Value** | 0.049 | 0.003 |
| **Reference Value** | 0.048 | 0.003 |
| **Robust Average** | 0.041 | 0.012 |
| **Median** | 0.0400 | 0.0072 |
| **Mean** | 0.045 | |
| **N** | 13 | |
| **Max** | 0.1 | |
| **Min** | 0.01 | |
| **Robust SD** | 0.017 | |
| **Robust CV** | 42% | |

Assigned value is the reference value as determined by IDMS.


Kernel Density
Density
Result
Results: S2 - Deltamethrin
Assigned Value = 0.048 ± 0.003 mg/kg
Results (mg/kg)
Laboratory
6 9 3 8 7 14 2 11 16 4 12 10 1 5 13 15 Md RA HV RV SV


z-Scores: S2 - Deltamethrin
Target Standard Deviation for Proficiency Assessment 0.0072 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
6 9 3 8 7 14 2 11 16 4 12 10 1
-3.8
-2.1
-2.0
-1.5
-1.4
-1.1
-1.0
-0.4
0.3
0.3

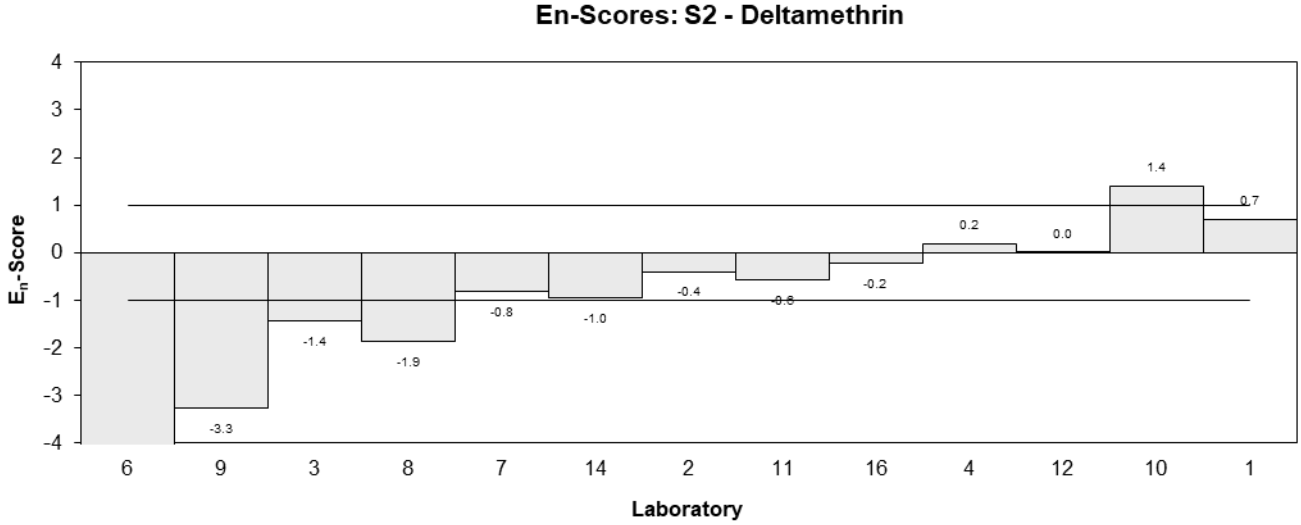

En-Scores: S2 - Deltamethrin
En-Score
Laboratory
6 9 3 8 7 14 2 11 16 4 12 10 1
-3.3
-1.4
-1.9
-0.8
-1.0
-0.4
-0.6
-0.2
0.2
0.0
1.4
0.7

Figure 8

Table 12

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Plum |
| **Analyte** | Difenoconazole |
| **Unit** | mg/kg |

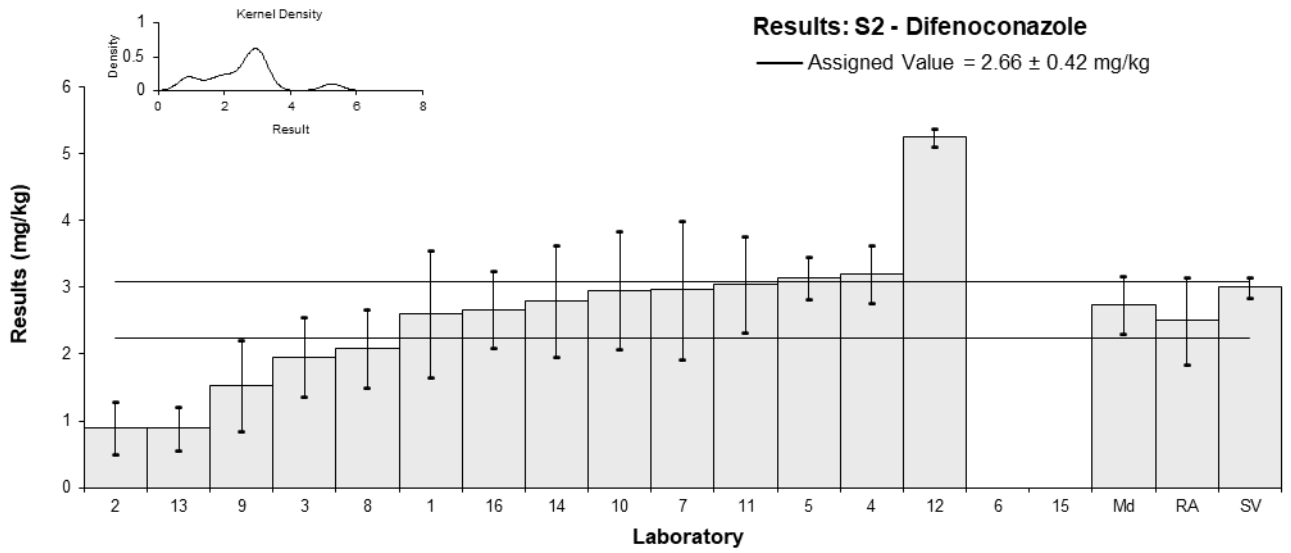
**Participant Results**

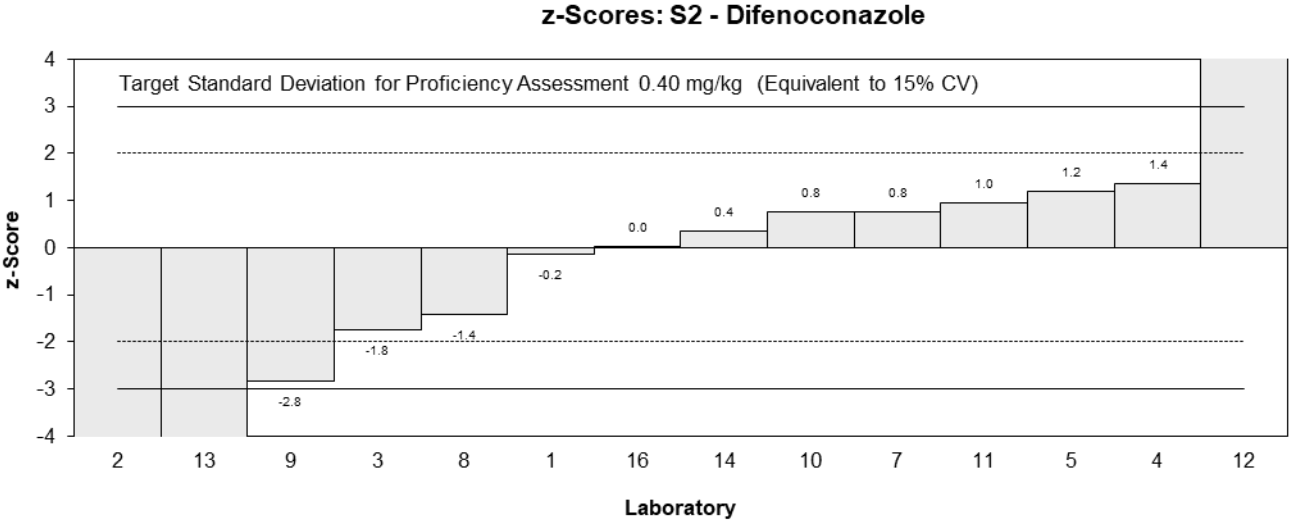
| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 2.6 | 0.95 | 87 | -0.15 | -0.06 |
| **2*** | 0.89 | 0.39 | 89 | -4.44 | -3.09 |
| **3** | 1.96 | 0.59 | 82 | -1.75 | -0.97 |
| **4** | 3.2 | 0.43 | 87 | 1.35 | 0.90 |
| **5** | 3.14 | 0.314 | 86.23 | 1.20 | 0.92 |
| **6** | NT | NT | NT | | |
| **7** | 2.968 | 1.039 | 82 | 0.77 | 0.27 |
| **8** | 2.090 | 0.585 | 76 | -1.43 | -0.79 |
| **9** | 1.53 | 0.69 | 91 | -2.83 | -1.40 |
| **10** | 2.96 | 0.89 | 105 | 0.75 | 0.30 |
| **11** | 3.04 | 0.72 | 80 | 0.95 | 0.46 |
| **12*** | 5.25 | 0.13 | 83 | 6.49 | 5.89 |
| **13*** | 0.89 | 0.33 | 108 | -4.44 | -3.31 |
| **14** | 2.8 | 0.84 | 80 | 0.35 | 0.15 |
| **15** | NT | NT | NT | | |
| **16** | 2.67 | 0.57 | 103 | 0.03 | 0.01 |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 2.66 | 0.42 |
| **Spike Value** | 3.00 | 0.15 |
| **Robust Average** | 2.50 | 0.65 |
| **Median** | 2.74 | 0.43 |
| **Mean** | 2.57 | |
| **N** | 14 | |
| **Max** | 5.25 | |
| **Min** | 0.89 | |
| **Robust SD** | 0.97 | |
| **Robust CV** | 39% | |


Kernel Density
Density
Result
Results: S2 - Difenoconazole
Assigned Value = 2.66 ± 0.42 mg/kg
Results (mg/kg)
Laboratory
2 13 9 3 8 1 16 14 10 7 11 5 4 12 6 15 Md RA SV


z-Scores: S2 - Difenoconazole
Target Standard Deviation for Proficiency Assessment 0.40 mg/kg (Equivalent to 15% CV)
z-Score
-2.8 -1.8 -1.4 -0.2 0.0 0.4 0.8 0.8 1.0 1.2 1.4
Laboratory
2 13 9 3 8 1 16 14 10 7 11 5 4 12

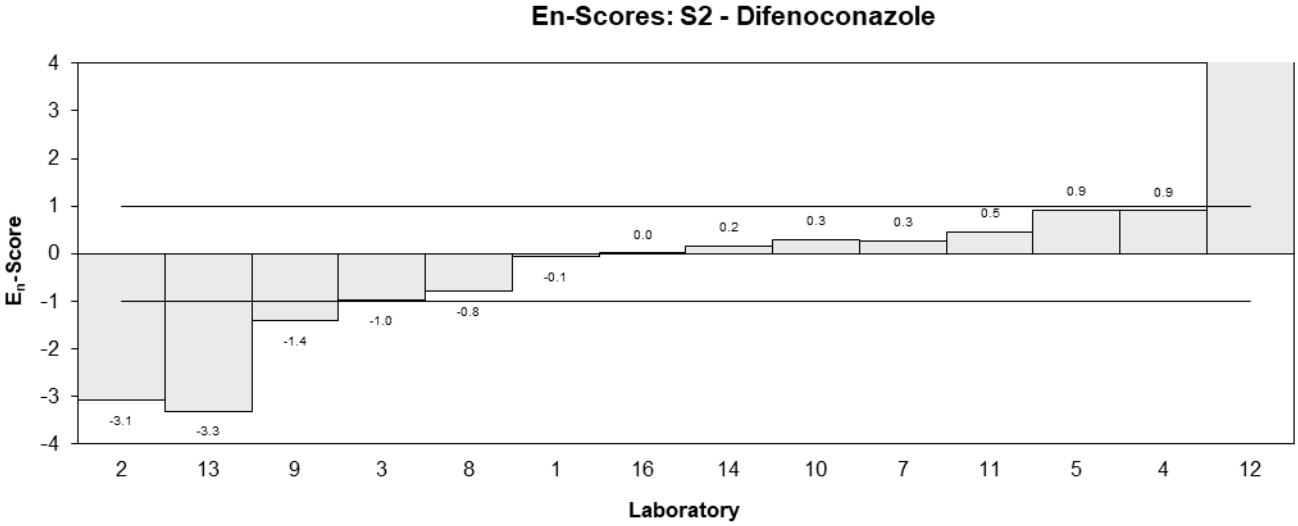

En-Scores: S2 - Difenoconazole
En-Score
-3.1 -3.3 -1.4 -1.0 -0.8 -0.1 0.0 0.2 0.3 0.3 0.5 0.9 0.9
Laboratory
2 13 9 3 8 1 16 14 10 7 11 5 4 12

Figure 9

Table 13

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Plum |
| **Analyte** | Endosulfan sulfate |
| **Unit** | mg/kg |

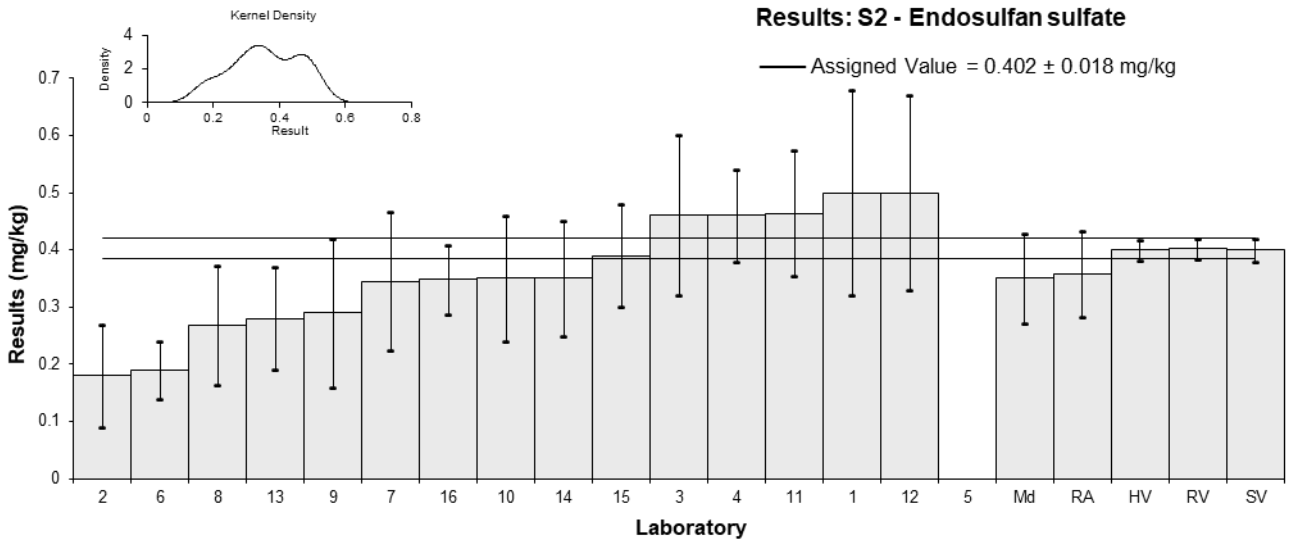
**Participant Results**

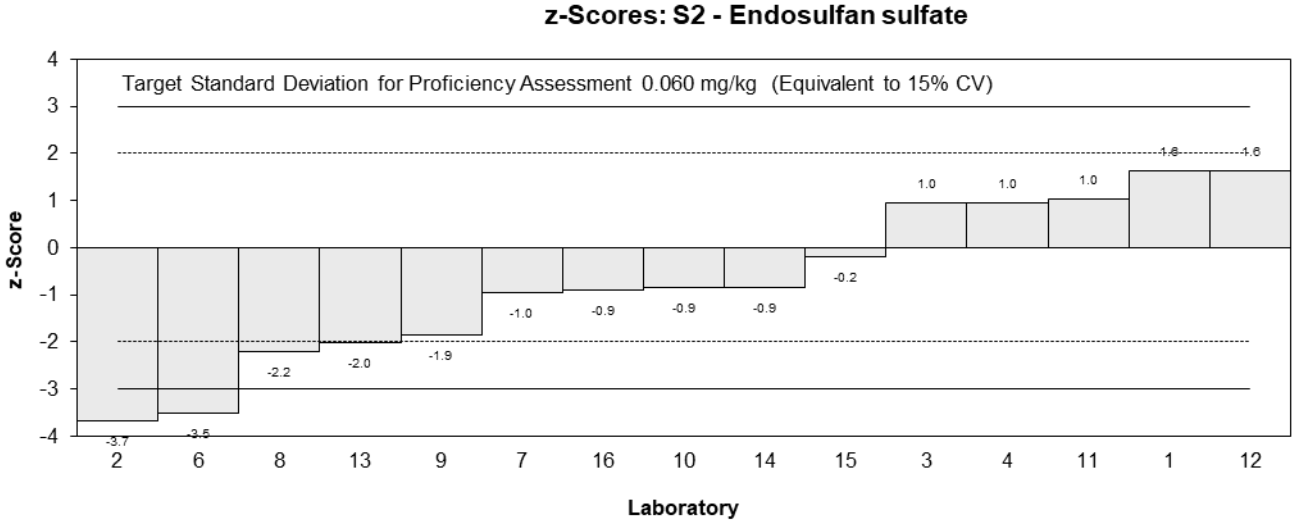
| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.50 | 0.18 | 102 | 1.63 | 0.54 |
| **2** | 0.18 | 0.09 | 120 | -3.68 | -2.42 |
| **3** | 0.46 | 0.14 | 112.50 | 0.96 | 0.41 |
| **4** | 0.46 | 0.08 | 104 | 0.96 | 0.71 |
| **5** | NT | NT | NT | | |
| **6** | 0.19 | 0.05 | NR | -3.52 | -3.99 |
| **7** | 0.345 | 0.121 | 80 | -0.95 | -0.47 |
| **8** | 0.268 | 0.105 | 113 | -2.22 | -1.26 |
| **9** | 0.29 | 0.13 | 82 | -1.86 | -0.85 |
| **10** | 0.35 | 0.11 | 92 | -0.86 | -0.47 |
| **11** | 0.464 | 0.11 | 105 | 1.03 | 0.56 |
| **12** | 0.5 | 0.17 | 97 | 1.63 | 0.57 |
| **13** | 0.28 | 0.09 | 99 | -2.02 | -1.33 |
| **14** | 0.35 | 0.1 | 82 | -0.86 | -0.51 |
| **15** | 0.39 | 0.09 | 98 | -0.20 | -0.13 |
| **16** | 0.348 | 0.06 | 98 | -0.90 | -0.86 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.402 | 0.018 |
| **Spike Value** | 0.400 | 0.020 |
| **Homogeneity Value** | 0.400 | 0.018 |
| **Reference Value** | 0.402 | 0.018 |
| **Robust Average** | 0.358 | 0.076 |
| **Median** | 0.350 | 0.078 |
| **Mean** | 0.358 | |
| **N** | 15 | |
| **Max** | 0.5 | |
| **Min** | 0.18 | |
| **Robust SD** | 0.12 | |
| **Robust CV** | 33% | |

Assigned value is the reference value as determined by IDMS.


Results: S2 - Endosulfan sulfate
Kernel Density
Density
Result
Assigned Value = 0.402 ± 0.018 mg/kg
Results (mg/kg)
Laboratory
2 6 8 13 9 7 16 10 14 15 3 4 11 1 12 5 Md RA HV RV SV


z-Scores: S2 - Endosulfan sulfate
Target Standard Deviation for Proficiency Assessment 0.060 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
2 6 8 13 9 7 16 10 14 15 3 4 11 1 12

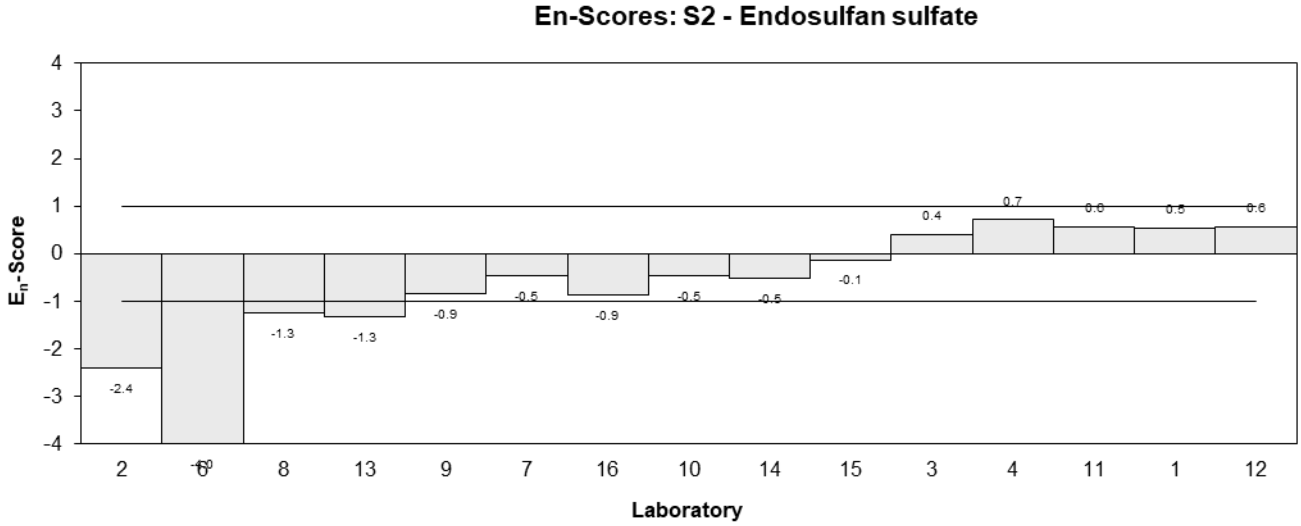

En-Scores: S2 - Endosulfan sulfate
En-Score
Laboratory
2 6 8 13 9 7 16 10 14 15 3 4 11 1 12

Figure 10

Table 14

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Plum |
| **Analyte** | Imidacloprid |
| **Unit** | mg/kg |

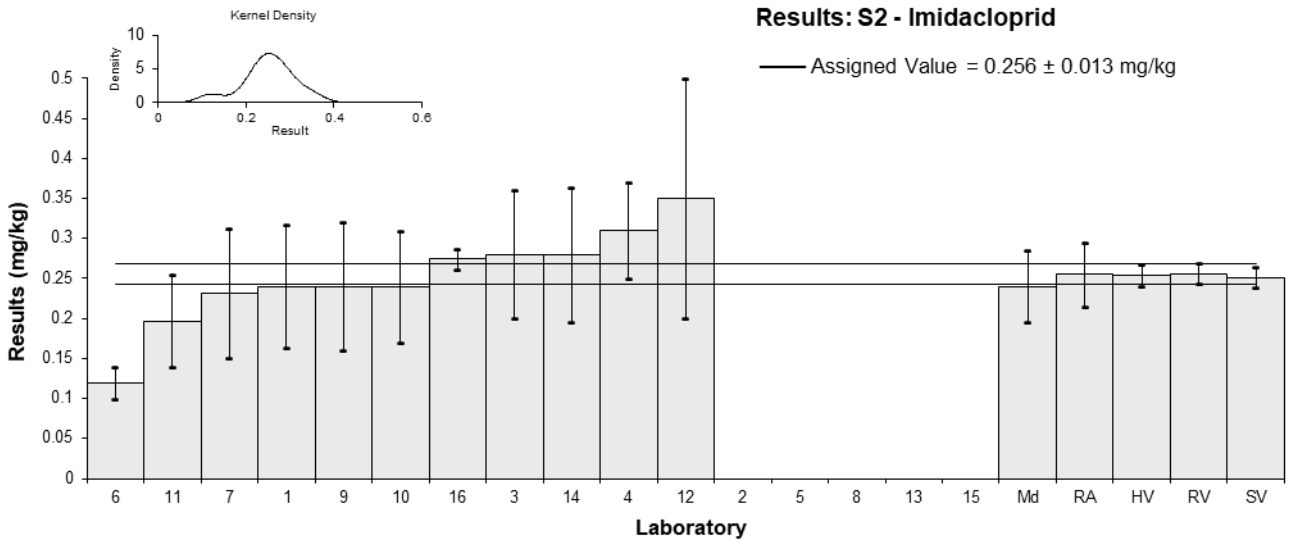
**Participant Results**

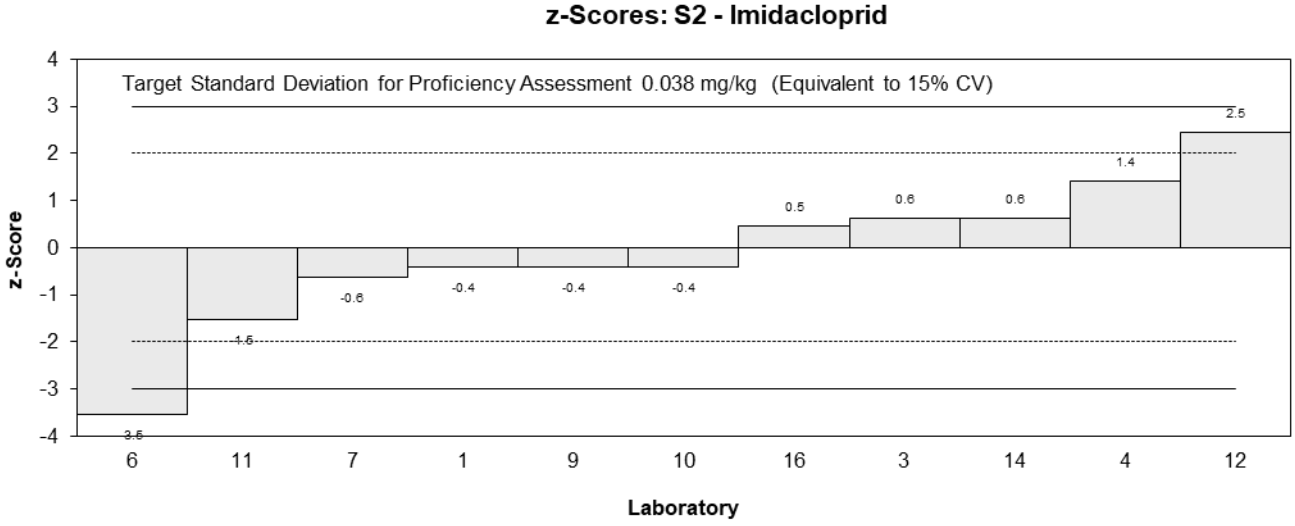
| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.24 | 0.077 | 78 | -0.42 | -0.20 |
| **2** | NT | NT | NT | | |
| **3** | 0.28 | 0.08 | 85 | 0.63 | 0.30 |
| **4** | 0.31 | 0.06 | 98 | 1.41 | 0.88 |
| **5** | NT | NT | NT | | |
| **6** | 0.12 | 0.02 | NR | -3.54 | -5.70 |
| **7** | 0.232 | 0.081 | 71 | -0.62 | -0.29 |
| **8** | NT | NT | NT | | |
| **9** | 0.24 | 0.08 | 114 | -0.42 | -0.20 |
| **10** | 0.24 | 0.07 | 91 | -0.42 | -0.22 |
| **11** | 0.197 | 0.058 | 48 | -1.54 | -0.99 |
| **12** | 0.35 | 0.15 | 85 | 2.45 | 0.62 |
| **13** | NT | NT | NT | | |
| **14** | 0.28 | 0.084 | 98 | 0.63 | 0.28 |
| **15** | NT | NT | NT | | |
| **16** | 0.274 | 0.013 | 108.6 | 0.47 | 0.98 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.256 | 0.013 |
| **Spike Value** | 0.251 | 0.013 |
| **Homogeneity Value** | 0.254 | 0.013 |
| **Reference Value** | 0.256 | 0.013 |
| **Robust Average** | 0.255 | 0.040 |
| **Median** | 0.240 | 0.045 |
| **Mean** | 0.251 | |
| **N** | 11 | |
| **Max** | 0.35 | |
| **Min** | 0.12 | |
| **Robust SD** | 0.053 | |
| **Robust CV** | 21% | |

Assigned value is the reference value as determined by IDMS.


Results: S2 - Imidacloprid
Assigned Value = 0.256 ± 0.013 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
6 11 7 1 9 10 16 3 14 4 12 2 5 8 13 15 Md RA HV RV SV


z-Scores: S2 - Imidacloprid
Target Standard Deviation for Proficiency Assessment 0.038 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
6 11 7 1 9 10 16 3 14 4 12
-3.6
-1.5
-0.6
-0.4
-0.4
-0.4
0.5
0.6
0.6
1.4
2.5

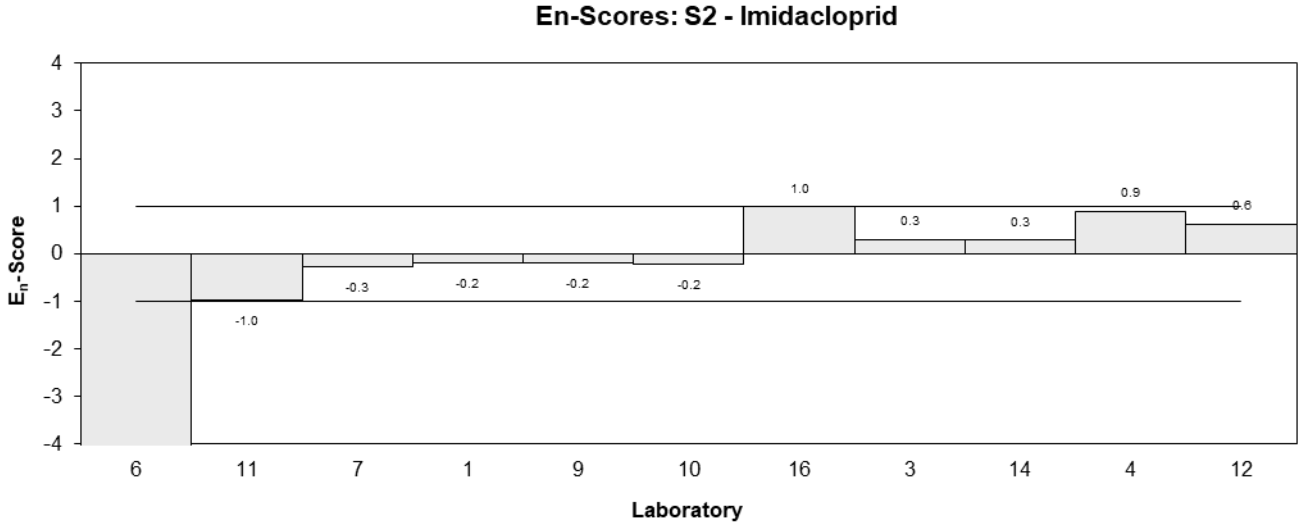

En-Scores: S2 - Imidacloprid
En-Score
Laboratory
6 11 7 1 9 10 16 3 14 4 12
-1.0
-0.3
-0.2
-0.2
-0.2
1.0
0.3
0.3
0.9
0.6

Figure 11

Table 15

**Sample Details**

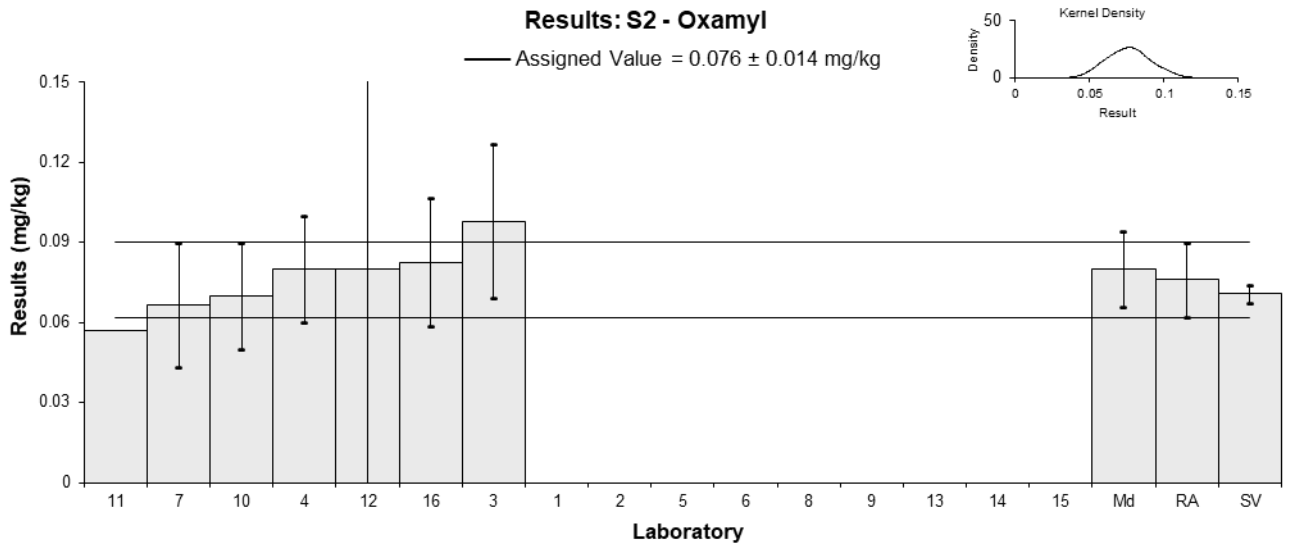
| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Plum |
| **Analyte** | Oxamyl |
| **Unit** | mg/kg |

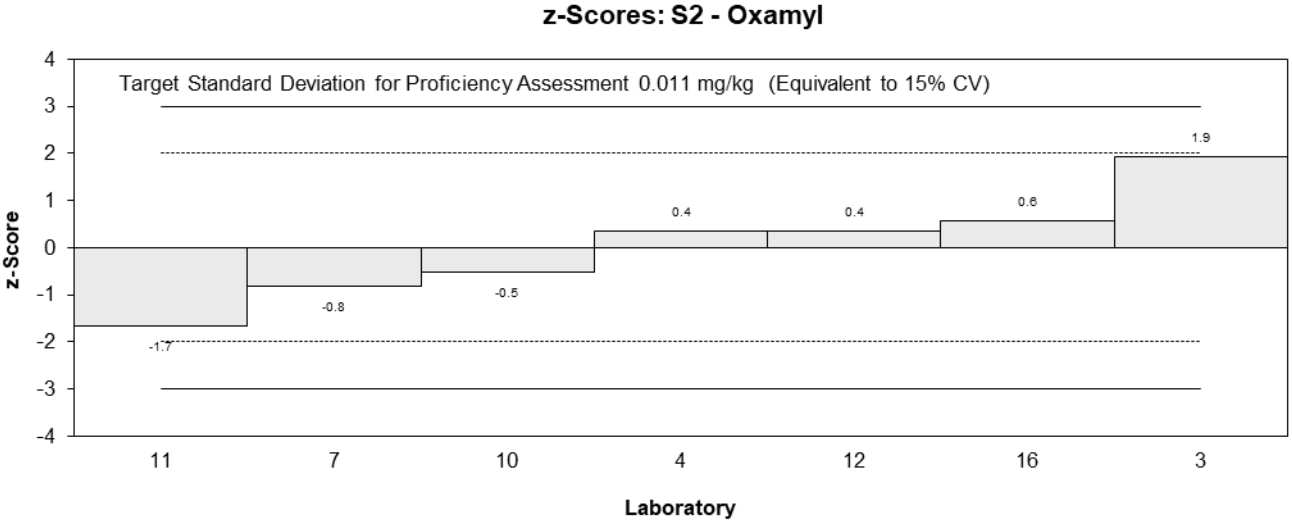
**Participant Results**

| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | NT | NT | NT | | |
| **2** | NT | NT | NT | | |
| **3** | 0.098 | 0.029 | 63 | 1.93 | 0.68 |
| **4** | 0.08 | 0.02 | 89 | 0.35 | 0.16 |
| **5** | NT | NT | NT | | |
| **6** | NT | NT | NT | | |
| **7** | 0.0665 | 0.0233 | 94 | -0.83 | -0.35 |
| **8** | NT | NT | NT | | |
| **9** | NT | NT | NT | | |
| **10** | 0.07 | 0.02 | 107 | -0.53 | -0.25 |
| **11** | 0.057 | NR | 61 | -1.67 | -1.36 |
| **12** | 0.08 | 0.24 | 96 | 0.35 | 0.02 |
| **13** | NT | NT | NT | | |
| **14** | <0.01 | NR | NR | | |
| **15** | NT | NT | NT | | |
| **16** | 0.0825 | 0.024 | 87.3 | 0.57 | 0.23 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.076 | 0.014 |
| **Spike Value** | 0.0707 | 0.0035 |
| **Robust Average** | 0.076 | 0.014 |
| **Median** | 0.080 | 0.014 |
| **Mean** | 0.0763 | |
| **N** | 7 | |
| **Max** | 0.098 | |
| **Min** | 0.057 | |
| **Robust SD** | 0.015 | |
| **Robust CV** | 20% | |


Results: S2 - Oxamyl
Assigned Value = 0.076 ± 0.014 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
11 7 10 4 12 16 3 1 2 5 6 8 9 13 14 15 Md RA SV


z-Scores: S2 - Oxamyl
Target Standard Deviation for Proficiency Assessment 0.011 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
11 7 10 4 12 16 3
-1.7
-0.8
-0.5
0.4
0.4
0.6
1.9

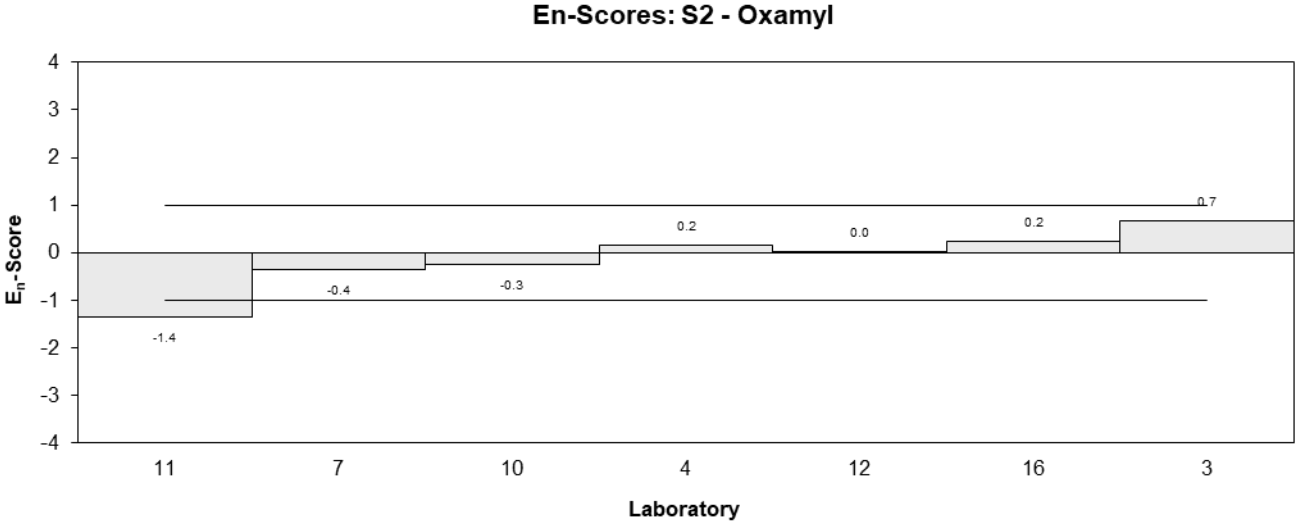

En-Scores: S2 - Oxamyl
En-Score
Laboratory
11 7 10 4 12 16 3
-1.4
-0.4
-0.3
0.2
0.0
0.2
0.7

Figure 12

Table 16

**Sample Details**

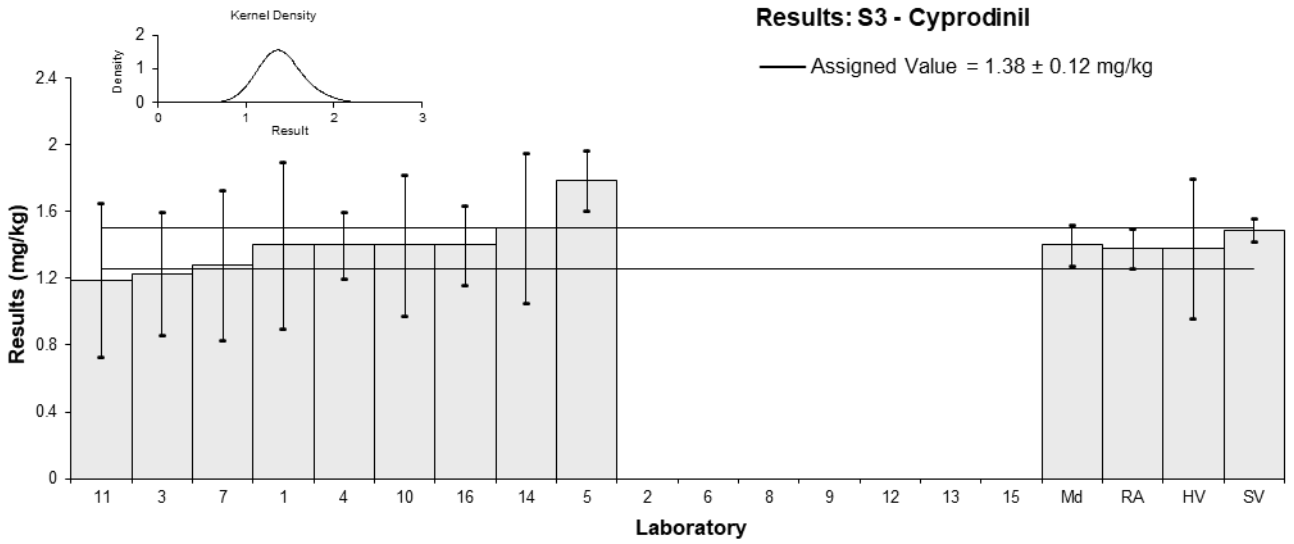
| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | Garlic |
| **Analyte** | Cyprodinil |
| **Unit** | mg/kg |

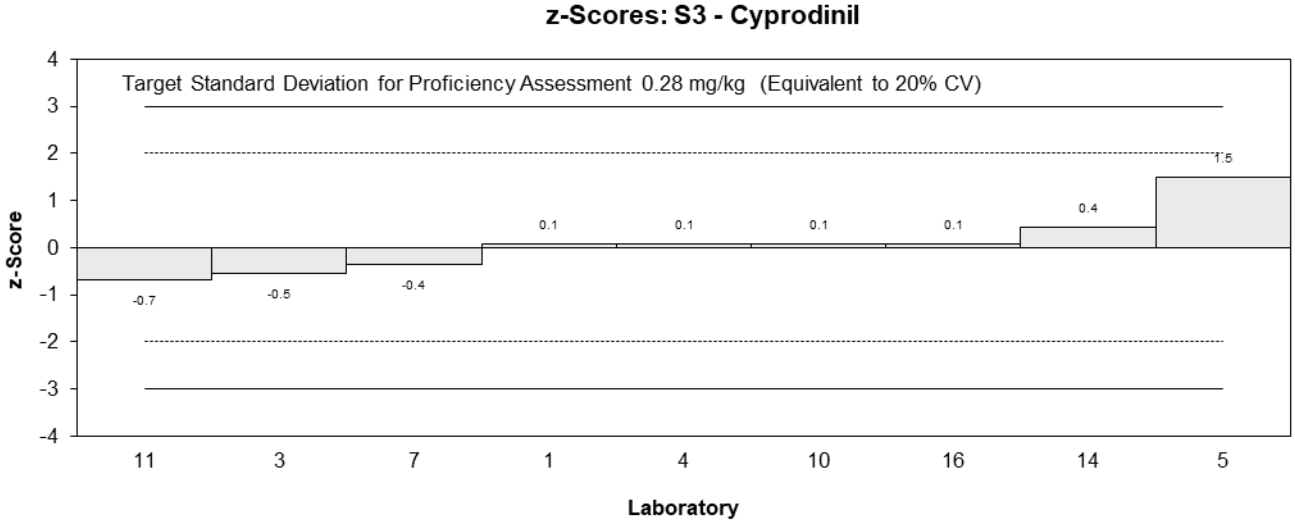
**Participant Results**

| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 1.4 | 0.50 | 97 | 0.07 | 0.04 |
| **2** | NT | NT | NT | | |
| **3** | 1.23 | 0.37 | 102.50 | -0.54 | -0.39 |
| **4** | 1.4 | 0.2 | 95 | 0.07 | 0.09 |
| **5** | 1.79 | 0.179 | 87.77 | 1.49 | 1.90 |
| **6** | <0.01 | NR | NR | | |
| **7** | 1.283 | 0.449 | 80 | -0.35 | -0.21 |
| **8** | NT | NT | NT | | |
| **9** | NT | NT | NT | | |
| **10** | 1.40 | 0.42 | 108 | 0.07 | 0.05 |
| **11** | 1.19 | 0.46 | 80 | -0.69 | -0.40 |
| **12** | NR | NR | NR | | |
| **13** | NT | NT | NT | | |
| **14** | 1.5 | 0.45 | 97 | 0.43 | 0.26 |
| **15** | NT | NT | NT | | |
| **16** | 1.4 | 0.24 | 75 | 0.07 | 0.07 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1.38 | 0.12 |
| **Spike Value** | 1.49 | 0.07 |
| **Homogeneity Value** | 1.38 | 0.42 |
| **Robust Average** | 1.38 | 0.12 |
| **Median** | 1.40 | 0.12 |
| **Mean** | 1.40 | |
| **N** | 9 | |
| **Max** | 1.79 | |
| **Min** | 1.19 | |
| **Robust SD** | 0.14 | |
| **Robust CV** | 11% | |


Kernel Density
Density
Result
Results: S3 - Cyprodinil
Assigned Value = 1.38 ± 0.12 mg/kg
Results (mg/kg)
Laboratory
11 3 7 1 4 10 16 14 5 2 6 8 9 12 13 15 Md RA HV SV


z-Scores: S3 - Cyprodinil
Target Standard Deviation for Proficiency Assessment 0.28 mg/kg (Equivalent to 20% CV)
z-Score
-0.7 -0.5 -0.4 0.1 0.1 0.1 0.1 0.4 1.5
Laboratory
11 3 7 1 4 10 16 14 5

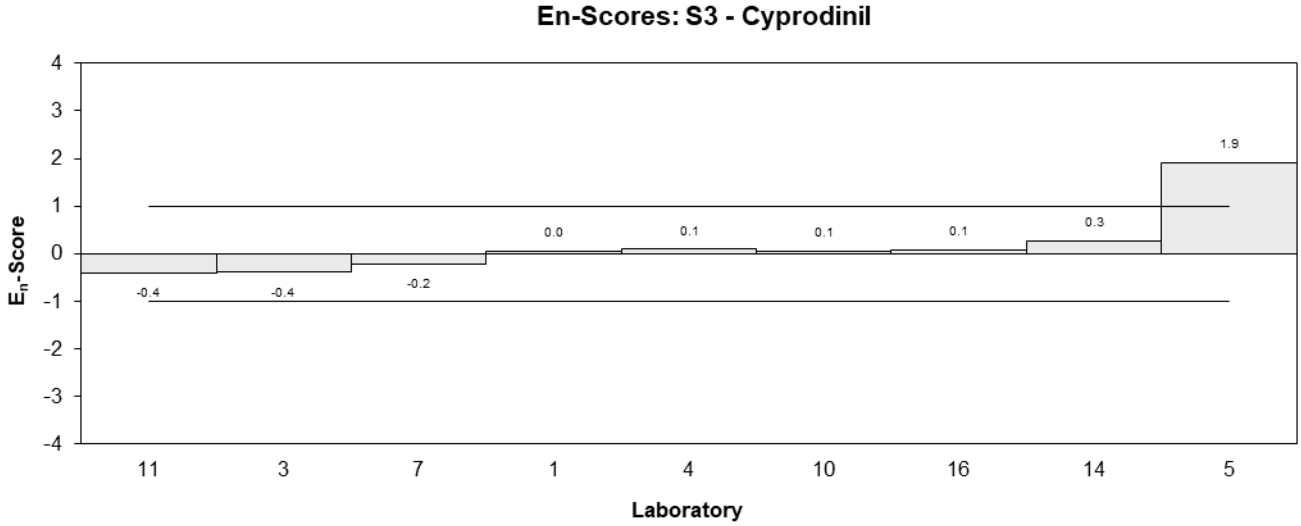

En-Scores: S3 - Cyprodinil
En-Score
-0.4 -0.4 -0.2 0.0 0.1 0.1 0.1 0.3 1.9
Laboratory
11 3 7 1 4 10 16 14 5

Figure 13

Table 17

**Sample Details**

| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | Garlic |
| **Analyte** | Endosulfan sulfate |
| **Unit** | mg/kg |

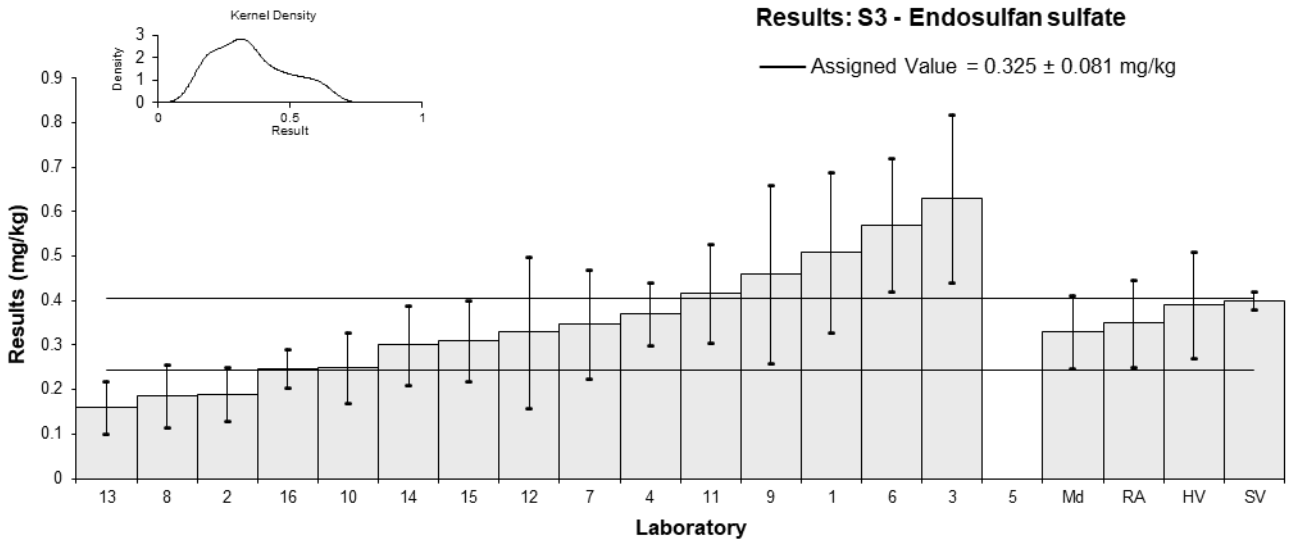
**Participant Results**

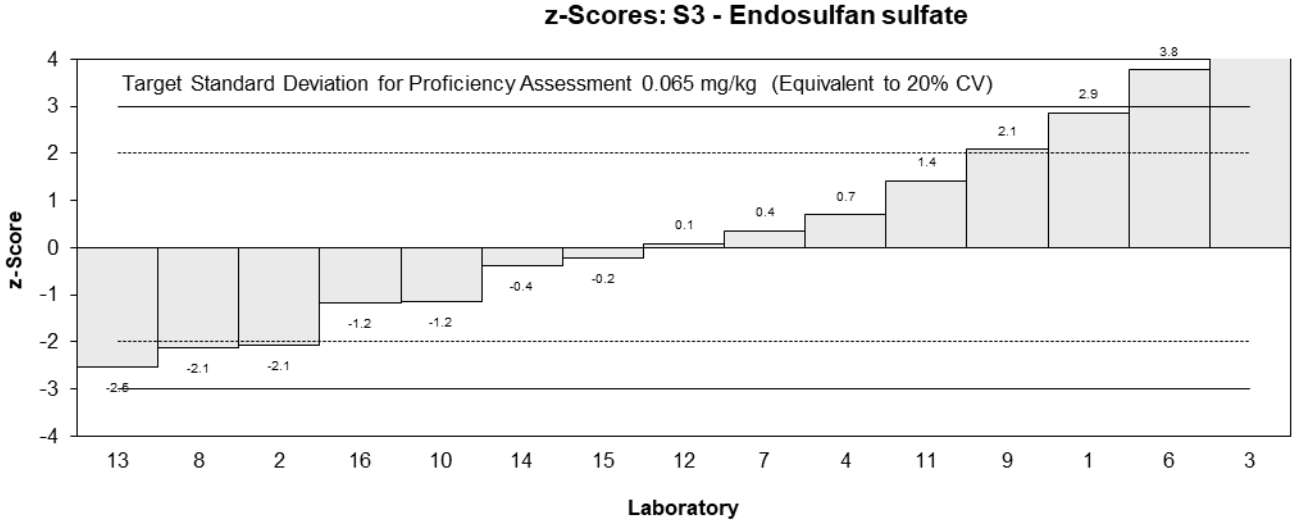
| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.51 | 0.18 | 102 | 2.85 | 0.94 |
| **2** | 0.19 | 0.06 | 113 | -2.08 | -1.34 |
| **3*** | 0.63 | 0.19 | 124.50 | 4.69 | 1.48 |
| **4** | 0.37 | 0.07 | 106 | 0.69 | 0.42 |
| **5** | NT | NT | NT | | |
| **6*** | 0.57 | 0.15 | NR | 3.77 | 1.44 |
| **7** | 0.348 | 0.122 | 82 | 0.35 | 0.16 |
| **8** | 0.187 | 0.071 | 70 | -2.12 | -1.28 |
| **9** | 0.46 | 0.2 | 123 | 2.08 | 0.63 |
| **10** | 0.25 | 0.08 | 89 | -1.15 | -0.66 |
| **11** | 0.417 | 0.11 | 91 | 1.42 | 0.67 |
| **12** | 0.33 | 0.17 | 97 | 0.08 | 0.03 |
| **13*** | 0.16 | 0.06 | 97 | -2.54 | -1.64 |
| **14** | 0.30 | 0.09 | 102 | -0.38 | -0.21 |
| **15** | 0.31 | 0.09 | 101 | -0.23 | -0.12 |
| **16** | 0.248 | 0.044 | 62 | -1.18 | -0.84 |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.325 | 0.081 |
| **Spike Value** | 0.400 | 0.020 |
| **Homogeneity Value** | 0.39 | 0.12 |
| **Robust Average** | 0.349 | 0.099 |
| **Median** | 0.330 | 0.083 |
| **Mean** | 0.352 | |
| **N** | 15 | |
| **Max** | 0.63 | |
| **Min** | 0.16 | |
| **Robust SD** | 0.15 | |
| **Robust CV** | 44% | |


Kernel Density
Density
Result
Results: S3 - Endosulfan sulfate
Assigned Value = 0.325 ± 0.081 mg/kg
Results (mg/kg)
13 8 2 16 10 14 15 12 7 4 11 9 1 6 3 5 Md RA HV SV
Laboratory


z-Scores: S3 - Endosulfan sulfate
Target Standard Deviation for Proficiency Assessment 0.065 mg/kg (Equivalent to 20% CV)
z-Score
-2.6 -2.1 -2.1 -1.2 -1.2 -0.4 -0.2 0.1 0.4 0.7 1.4 2.1 2.9 3.8
13 8 2 16 10 14 15 12 7 4 11 9 1 6 3
Laboratory

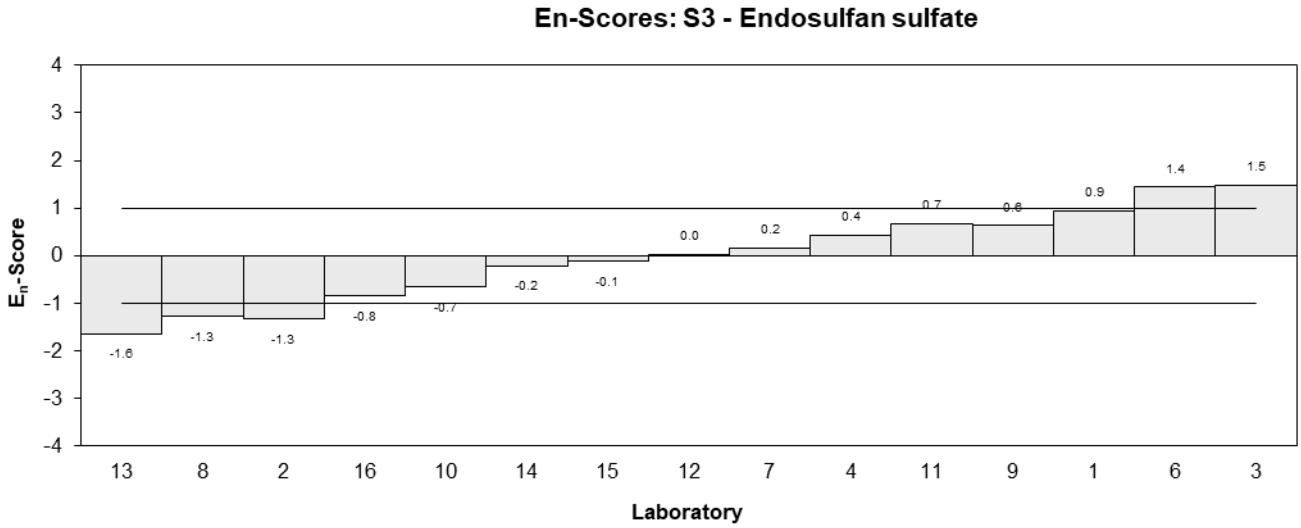

En-Scores: S3 - Endosulfan sulfate
En-Score
-1.6 -1.3 -1.3 -0.8 -0.7 -0.2 -0.1 0.0 0.2 0.4 0.7 0.6 0.9 1.4 1.5
13 8 2 16 10 14 15 12 7 4 11 9 1 6 3
Laboratory

Figure 14

Table 18

**Sample Details**

| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | Garlic |
| **Analyte** | Maleic hydrazide |
| **Unit** | mg/kg |

**Participant Results**

| Lab. Code | Result | Uncertainty | Rec |
|---|---|---|---|
| **1** | NT | NT | NT |
| **2** | NT | NT | NT |
| **3** | 3.88 | 1.16 | 56 |
| **4** | NT | NT | NT |
| **5** | NT | NT | NT |
| **6** | NT | NT | NT |
| **7** | NT | NT | NT |
| **8** | NT | NT | NT |
| **9** | NT | NT | NT |
| **10** | 1.73 | 0.52 | 67 |
| **11** | NT | NT | NT |
| **12** | NT | NT | NT |
| **13** | NT | NT | NT |
| **14** | NT | NT | NT |
| **15** | NT | NT | NT |
| **16** | 3.99 | 1.2 | 70.5 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | Not Set | |
| **Spike Value** | 16.0 | 0.8 |
| **Robust Average** | NA (N<6) | |
| **Median** | 3.88 | 0.24 |
| **Mean** | 3.2 | |
| **N** | 3 | |
| **Max** | 3.99 | |
| **Min** | 1.73 | |
| **Robust SD** | NA (N<6) | |
| **Robust CV** | NA (N<6) | |

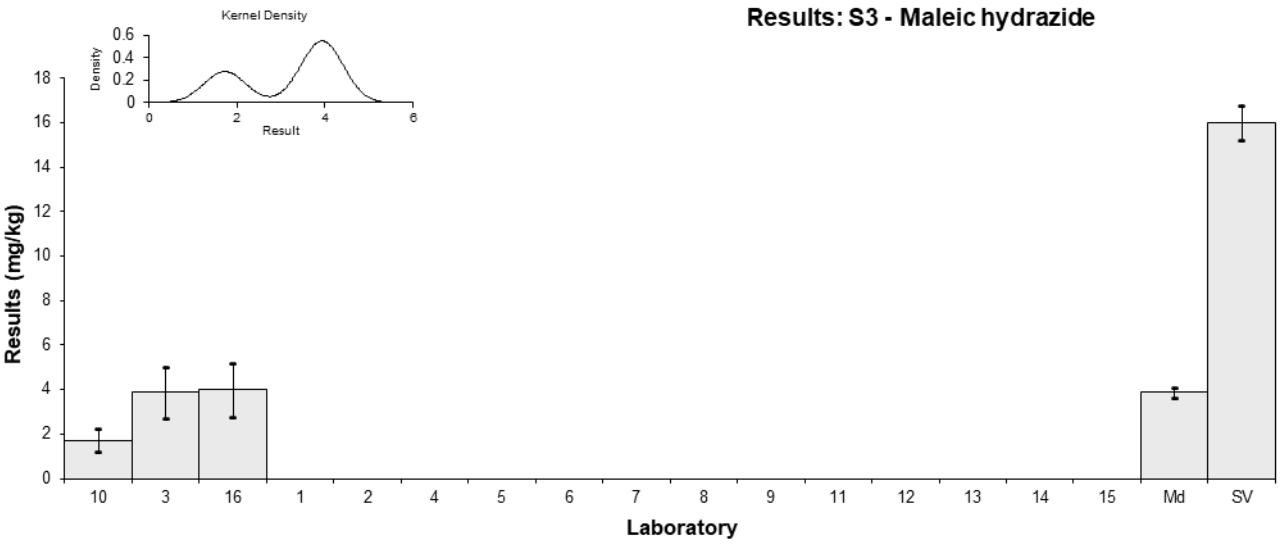

Results: S3 - Maleic hydrazide
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
10
3
16
1
2
4
5
6
7
8
9
11
12
13
14
15
Md
SV

Figure 15

Table 19

**Sample Details**

| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | Garlic |
| **Analyte** | Spirotetramat |
| **Unit** | mg/kg |

**Participant Results**

| Lab. Code | Result | Uncertainty | Rec |
|---|---|---|---|
| **1** | <0.01 | NR | NR |
| **2** | NT | NT | NT |
| **3** | NR | NR | NR |
| **4** | <0.01 | NR | 89 |
| **5** | < 0.01 | NR | NR |
| **6** | <0.1 | NR | NR |
| **7** | NT | NT | NT |
| **8** | NT | NT | NT |
| **9** | NT | NT | NT |
| **10** | NR | NR | 108 |
| **11** | 0.163 | NR | NR |
| **12** | NR | NR | NR |
| **13** | NT | NT | NT |
| **14** | 0.21 | 0.063 | 98 |
| **15** | NT | NT | NT |
| **16** | 0.742 | 0.14 | 112.1 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | Not Set | |
| **Spike Value** | 0.250 | 0.012 |
| **Robust Average** | NA (N<6) | |
| **Median** | 0.21 | 0.10 |
| **Mean** | 0.37 | |
| **N** | 3 | |
| **Max** | 0.742 | |
| **Min** | 0.163 | |
| **Robust SD** | NA (N<6) | |
| **Robust CV** | NA (N<6) | |

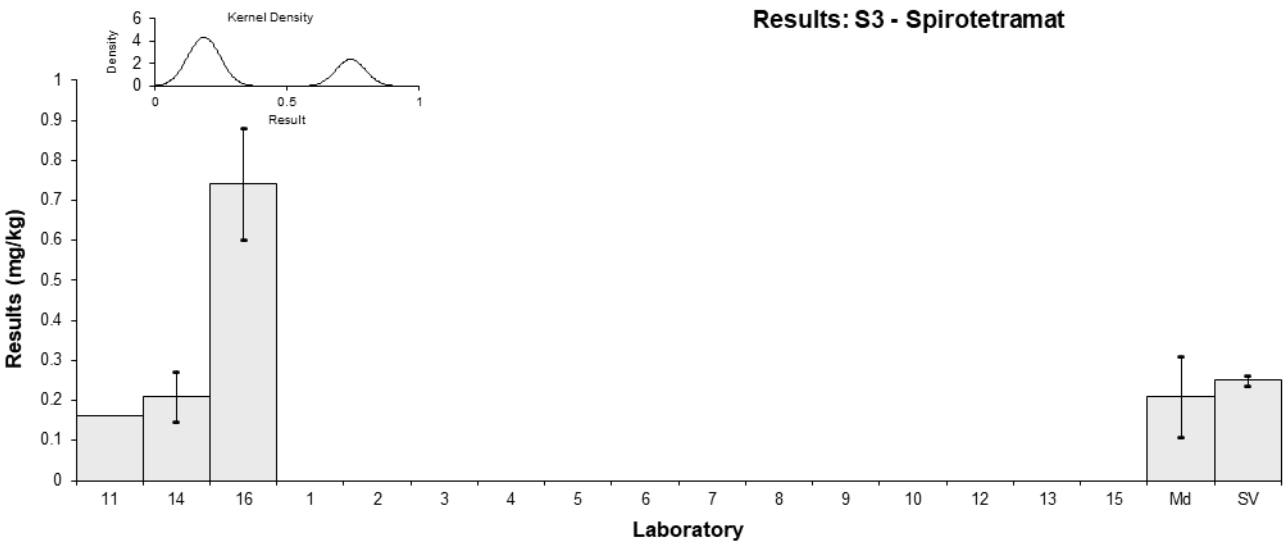

Results: S3 - Spirotetramat
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
11
14
16
1
2
3
4
5
6
7
8
9
10
12
13
15
Md
SV

Figure 16

## 6 DISCUSSION OF RESULTS

### 6.1 Assigned Value

The assigned values for Sample S2 acephate, deltamethrin, endosulfan sulfate and imidacloprid were the reference values obtained using IDMS. The uncertainties of the reference values were estimated in accordance with the ISO GUM.[11] Additional details are given in Appendix 2.

**Traceability:** The reference values are traceable to the SI unit for mass (kg) through the Australian national standards for mass and the CRMs used as calibrators.

The assigned values for all other scored analytes were the robust averages of participants' results. If there were results less than 50% or greater than 150% of the robust average, these were excluded from the calculation of each assigned value.[3,4] The robust average and associated expanded uncertainties were calculated using the procedure described in ISO 13528.[7] The calculation of the expanded uncertainty for robust averages is presented in Appendix 3, using Sample S1 fenhexamid 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 Sample S3 maleic hydrazide and spirotetramat as there were too few numeric results reported, and also stability issues were observed for maleic hydrazide.

A comparison of the assigned values (or robust average if no assigned value was set) and the spiked values is presented in Table 20. Assigned values were between 81% and 107% of the spiked values, providing good support for the assigned values and evidence for the stability of these analytes in the test samples.

Table 20 Comparison of Assigned Values *(Robust Averages)* and Spiked Values

| Sample | Analyte | Assigned Value *(Robust Average)* (mg/kg) | Spiked Value (mg/kg) | Assigned Value *(Robust Average)* / Spiked Value (%) |
|---|---|---|---|---|
| S1 | Azoxystrobin | 0.593 | 0.600 | 99 |
| | Chlorpyrifos | 0.815 | 0.829 | 98 |
| | Difenoconazole | 0.84 | 1.01 | 83 |
| | Endosulfan sulfate | 0.383 | 0.400 | 96 |
| | Fenhexamid | 0.393 | 0.402 | 98 |
| S2 | Acephate | 0.050 | 0.0495 | 101 |
| | Deltamethrin | 0.048 | 0.0500 | 96 |
| | Difenoconazole | 2.66 | 3.00 | 89 |
| | Endosulfan sulfate | 0.402 | 0.400 | 101 |
| | Imidacloprid | 0.256 | 0.251 | 102 |
| | Oxamyl | 0.076 | 0.0707 | 107 |
| S3 | Cyprodinil | 1.38 | 1.49 | 93 |
| | Endosulfan sulfate | 0.325 | 0.400 | 81 |
| | Maleic hydrazide | *(3.2)* | 16.0 | *(20)* |
| | Spirotetramat | *(0.37)* | 0.250 | *(148)* |

## 6.2 Measurement Uncertainty Reported by Participants

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

Of 165 numeric results for the analytes of interest in this study, 163 (99%) were reported with an associated expanded MU. Participants used a wide variety of procedures to estimate their uncertainty (Table 3). One participant reported using the NATA Technical Note 33 as their guide; NATA no longer publishes this document.[12]

Laboratory **11** did not report uncertainties for two of their results, though they reported uncertainties for the rest of their results. This participant reported that they were accredited to ISO/IEC 17025.

The magnitude of the reported uncertainties for spiked analytes in this study was within the range 2.5% to 320% 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 over 50% may be too large and not fit for purpose. Of the 163 expanded uncertainties, 13 were less than 15% relative and seven were greater than 50% relative.

For this PT study, participants were requested to report absolute expanded uncertainties in units of mg/kg. Laboratories **3** and **10** reported all uncertainties as relative uncertainties (i.e. uncertainties were reported as '*x*%'); for consistency, these uncertainties have been converted to absolute uncertainties. Laboratory **12** reported one result with a small relative uncertainty of 2.5%, and three results with large relative uncertainties of 260%, 300% and 320%; this participant may have reported their uncertainties as relative instead of in units of mg/kg, however as their results were not reported as '*x*%', their uncertainties were not modified. In general, participants should ensure that they have reported their uncertainties with the correct units.

Uncertainties associated with results returning an acceptable *z*-score but an unacceptable $E_n$-score may have been underestimated.

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 the 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 2.968 ± 1.039 mg/kg, it is recommended to report 3.0 ± 1.0 mg/kg.[10]

## 6.3 z-Scores

Target SDs equivalent to 15% PCV were used to calculate *z*-scores for analytes in Samples S1 and S2. Target SDs equivalent to 20% PCV were used to calculate z-scores for analytes in Sample S3 as garlic was a new matrix introduced in this PT study. CVs predicted by the Thompson-Horwitz equation,[8] between-laboratory CVs obtained in this study, and target SDs (as PCV) are presented for comparison in Table 21.

Table 21 Comparison of Thompson-Horwitz CVs, Target SDs, and Between-Laboratory CV

| Sample | Analyte | Assigned Value *(Robust Average)* (mg/kg) | Thompson-Horwitz CV[a] (%) | Between-Laboratory CV[b] (%) | Target SD (as PCV) (%) |
|---|---|---|---|---|---|
| S1 | Azoxystrobin | 0.593 | 17 | 12 | 15 |
| | Chlorpyrifos | 0.815 | 16 | 15 | 15 |
| | Difenoconazole | 0.84 | 16 | 23 | 15 |
| | Endosulfan sulfate | 0.383 | 18 | 30 | 15 |
| | Fenhexamid | 0.393 | 18 | 15 | 15 |
| S2 | Acephate | 0.050 | 22 | 22 | 15 |
| | Deltamethrin | 0.048 | 22 | 42 | 15 |
| | Difenoconazole | 2.66 | 14 | 21 | 15 |
| | Endosulfan sulfate | 0.402 | 18 | 33 | 15 |
| | Imidacloprid | 0.256 | 20 | 21 | 15 |
| | Oxamyl | 0.076 | 22 | 20 | 15 |
| S3 | Cyprodinil | 1.38 | 15 | 11 | 20 |
| | Endosulfan sulfate | 0.325 | 19 | 34 | 20 |
| | Maleic hydrazide | *(3.2)* | 13 | 45 | Not Set |
| | Spirotetramat | *(0.37)* | 19 | 98 | Not Set |

[a] Calculated from the assigned value (robust average).

[b] Robust between-laboratory CV with outliers removed, if applicable.

Of 159 results for which *z*-scores were calculated, 117 (74%) returned $|z| \leq 2.0$, indicating an acceptable performance.

Laboratories **3**, **4**, **7**, **10**, **11**, **16** reported numeric results for all 13 scored analytes. Laboratories **7**, **11** and **16** achieved acceptable *z*-scores for all analytes. Three other participants received acceptable *z*-scores for all scored analytes that they reported results for: **14** (12), **5** (6) and **15** (4).

Two participants received unacceptable *z*-scores for all scored analytes that they reported results for: **13** (7) and **6** (5).

The dispersal of participants' *z*-scores is presented graphically by laboratory in Figure 17 and by analyte in Figure 18.

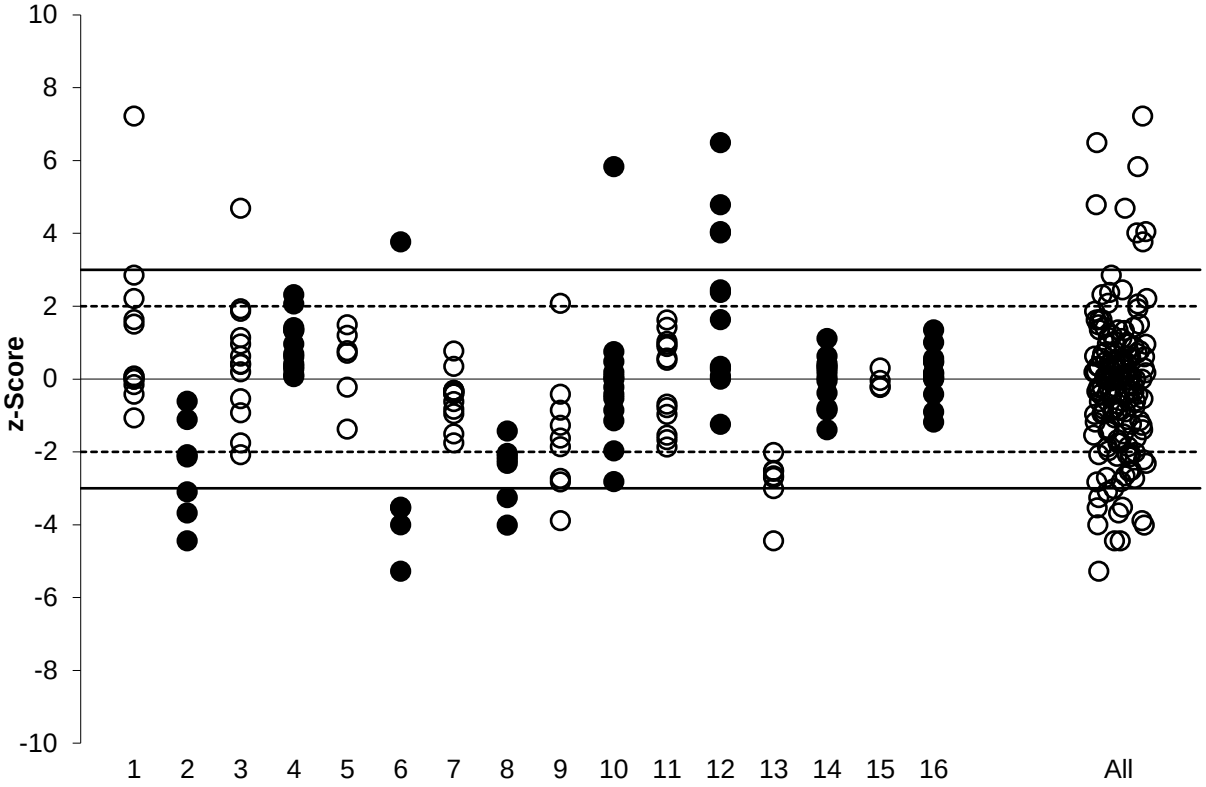



Figure 17 *z*-Score Dispersal by Laboratory

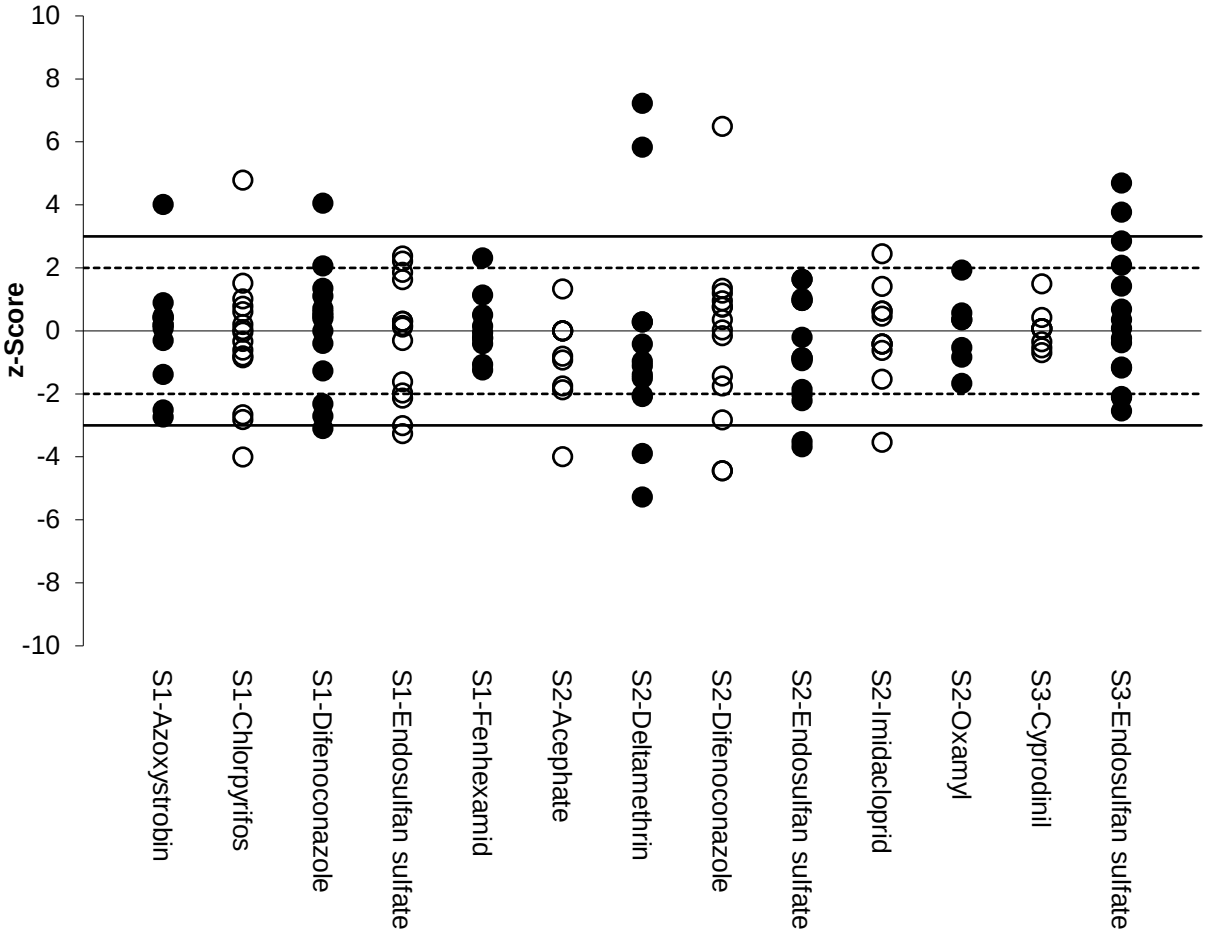



Figure 18 *z*-Score Dispersal by Analyte

## 6.4 $E_n$-Scores

$E_n$-scores can be interpreted in conjunction with *z*-scores, as an unacceptable $E_n$-score can either be caused by issues with measurement, or uncertainty, or both. Where a laboratory did not report an expanded uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the $E_n$-score.

Of 159 results for which $E_n$-scores were calculated, 118 (74%) returned $|E_n| < 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratory **16** achieved acceptable $E_n$-scores for all 13 scored analytes in this study. Three other participants received acceptable $E_n$-scores for all scored analytes that they reported results for: **1** (12), **14** (12) and **15** (4).

Two participants received unacceptable $E_n$-scores for all scored analytes that they reported results for: **13** (7) and **6** (5).

The dispersal of participants' $E_n$-scores is presented graphically by laboratory in Figure 19.

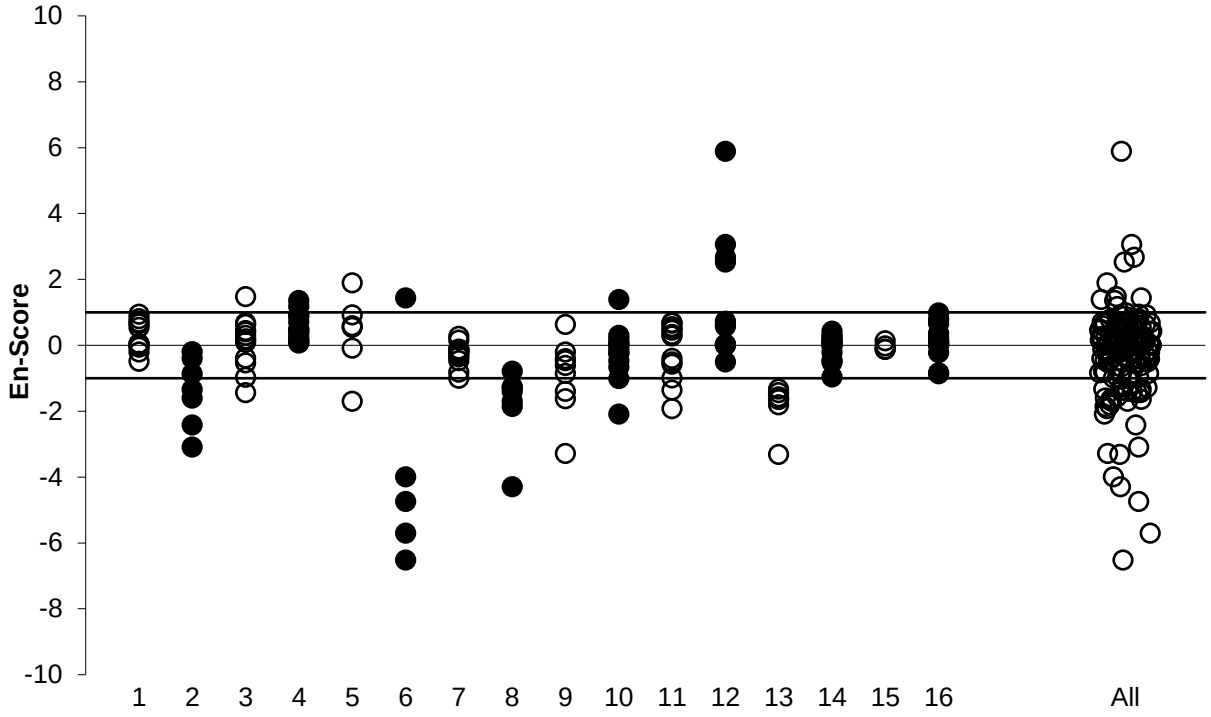



Figure 19 $E_n$-Score Dispersal by Laboratory

## 6.5 Range of Pesticides Analysed by Participants

Participants were given a list of analytes that could have been spiked into the samples (Table 1). Of these, 12 different analytes were spiked in this study, with two analytes being in multiple samples. Participants were not required to test for all analytes, and were requested to report 'NT' (for 'Not Tested') for pesticides they did not test for. A summary of participants' testing of the pesticides in this study is presented in Table 22 (participants have only been recorded as 'NT' if they reported 'NT' for that analyte across all samples).

Laboratories **3**, **10** and **16** reported that they tested for all analytes assessed in this study. For other participants, the proportion of analytes each participant tested for ranged from 25% to 92%.

All participants in this study tested for chlorpyrifos. For the other analytes, the proportion of participants testing for each analyte in this study ranged from 19% to 94%.

Table 22 Summary of Pesticides Analysed by Participants

| Analyte \ Lab. Code | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | Proportion of Participants (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Acephate | ✓ | NT | ✓ | ✓ | NT | ✓ | ✓ | NT | NT | ✓ | ✓ | ✓ | NT | ✓ | NT | ✓ | 63 |
| Azoxystrobin | ✓ | NT | ✓ | ✓ | ✓ | NT | ✓ | NT | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | NT | ✓ | 75 |
| Chlorpyrifos | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | 100 |
| Cyprodinil | ✓ | NT | ✓ | ✓ | ✓ | ✓ | ✓ | NT | NT | ✓ | ✓ | ✓ | NT | ✓ | NT | ✓ | 69 |
| Deltamethrin | ✓ | ✓ | ✓ | ✓ | NT | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | 94 |
| Difenoconazole | ✓ | ✓ | ✓ | ✓ | ✓ | NT | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | NT | ✓ | 88 |
| Endosulfan sulfate | ✓ | ✓ | ✓ | ✓ | NT | ✓[a] | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | 88 |
| Fenhexamid | ✓ | NT | ✓ | ✓ | ✓ | NT | ✓ | NT | NT | ✓ | ✓ | ✓ | NT | ✓ | NT | ✓ | 63 |
| Imidacloprid | ✓ | NT | ✓ | ✓ | NT | ✓ | ✓ | NT | ✓ | ✓ | ✓ | ✓ | NT | ✓ | NT | ✓ | 69 |
| Maleic hydrazide | NT | NT | ✓ | NT | NT | NT | NT | NT | NT | ✓ | NT | NT | NT | NT | NT | ✓ | 19 |
| Oxamyl | NT | NT | ✓ | ✓ | NT | NT | ✓ | NT | NT | ✓ | ✓ | ✓ | NT | ✓ | NT | ✓ | 50 |
| Spirotetramat | ✓ | NT | ✓ | ✓ | ✓ | ✓ | NT | NT | NT | ✓ | ✓ | ✓ | NT | ✓ | NT | ✓ | 63 |
| Proportion of Analytes (%) | 83 | 33 | 100 | 92 | 50 | 50 | 83 | 33 | 50 | 100 | 92 | 92 | 42 | 92 | 25 | 100 | |

[a] Laboratory **6** did not test for endosulfan sulfate in Sample S1, however they tested for this analyte in Samples S2 and S3.

## 6.6 False Negatives

Table 23 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 robust average and spiked value were significantly higher than the participants' LOR (i.e. the robust average 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 23 False Negatives

| Lab. Code | Sample | Analyte | Assigned Value *(Robust Average)* (mg/kg) | Spiked Value (mg/kg) | Result[a] (mg/kg) |
|---|---|---|---|---|---|
| 3 | S3 | Spirotetramat | *(0.37)* | 0.25 | NR |
| 6 | S3 | Cyprodinil | 1.38 | 1.49 | <0.01 |
| 10 | S3 | Spirotetramat | *(0.37)* | 0.25 | NR |
| 12 | S3 | Cyprodinil | 1.38 | 1.49 | NR |
| | | Spirotetramat | *(0.37)* | 0.25 | NR |
| 13 | S2 | Deltamethrin | 0.048 | 0.0500 | NR |
| 14 | S2 | Oxamyl | 0.076 | 0.0707 | <0.01 |
| 15 | S2 | Deltamethrin | 0.048 | 0.0500 | <0.01 |

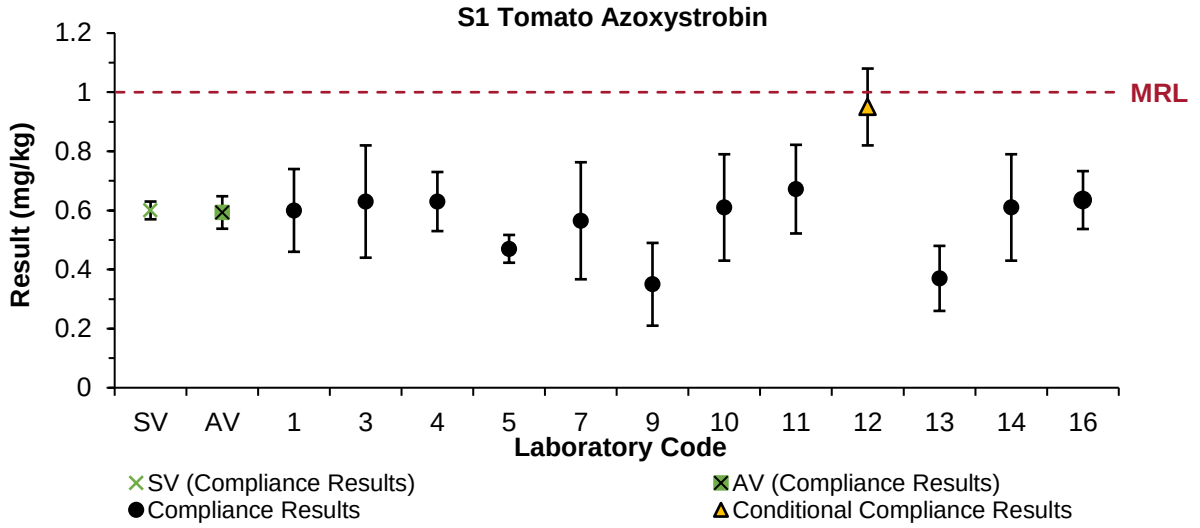
[a] NR results may or may not be false negatives, depending on the participant's actual LOR.

## 6.7 Fitness for Purpose of Pesticide Results

Internationally, there are several standards that set MRLs for various pesticides in different food products, typically to ensure that these products will not cause any adverse health effects when consumed. One standard that sets MRLs to food products in Australia is the Australia New Zealand Food Standards Code.[5] Laboratories need to ensure accurate measurements of these food products, so that their result correctly reflects whether a sample is compliant with the relevant MRL. For this study, six analytes had both spiked values and assigned values either above (non-compliant) or below (compliant) the relevant Australia New Zealand Food Standards Code MRL: Sample S1 azoxystrobin, chlorpyrifos and fenhexamid, Sample S2 imidacloprid and oxamyl, and Sample S3 cyprodinil.

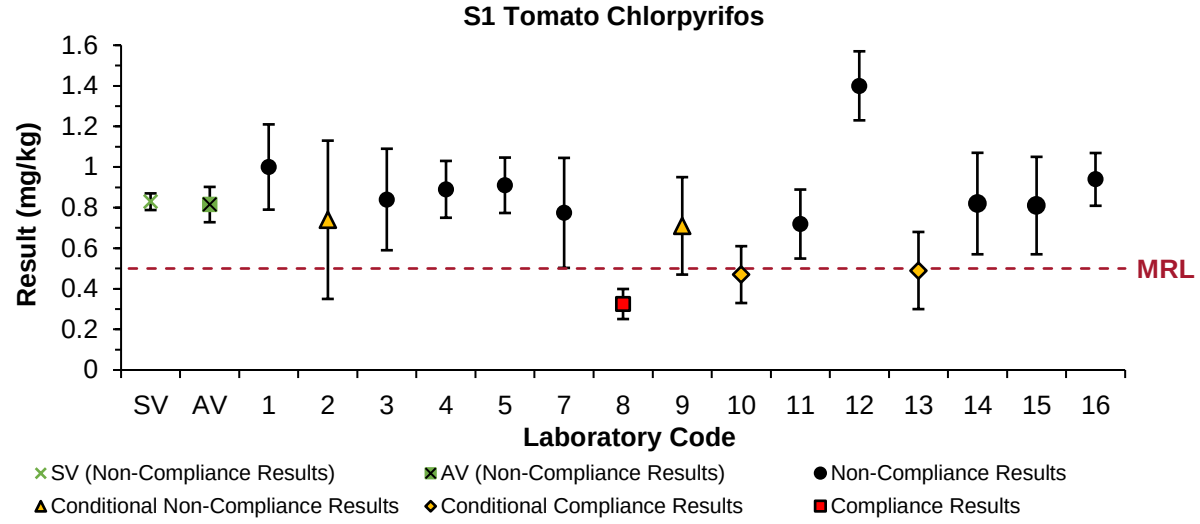
Figures 20 to 25 show comparisons of the spiked value (SV), assigned value (AV), participants' results, and MRLs for these six assessed analytes. Only numeric results have been included. In some cases, the MRL refers to the sum of a number of different permitted residues,[5] and not only the named analyte given here.

For the six analytes considered, most participants' results correctly reflected compliance or non-compliance. Of 64 results assessed, 55 (86%) gave the correct compliance status inclusive of uncertainty, and six (9%) gave conditionally correct compliance statuses (i.e. the result gave the correct compliance status but the uncertainty spanned the MRL). Laboratories **3**, **4**, **11** and **16** returned the correct compliance status, and Laboratory **7** returned either the correct or conditionally correct compliance status, for all six assessed analytes. Five participants returned the correct compliance status for all analytes they reported numeric results for: Laboratories **1** (5), **14** (5), **5** (4), **6** (1) and **15** (1).



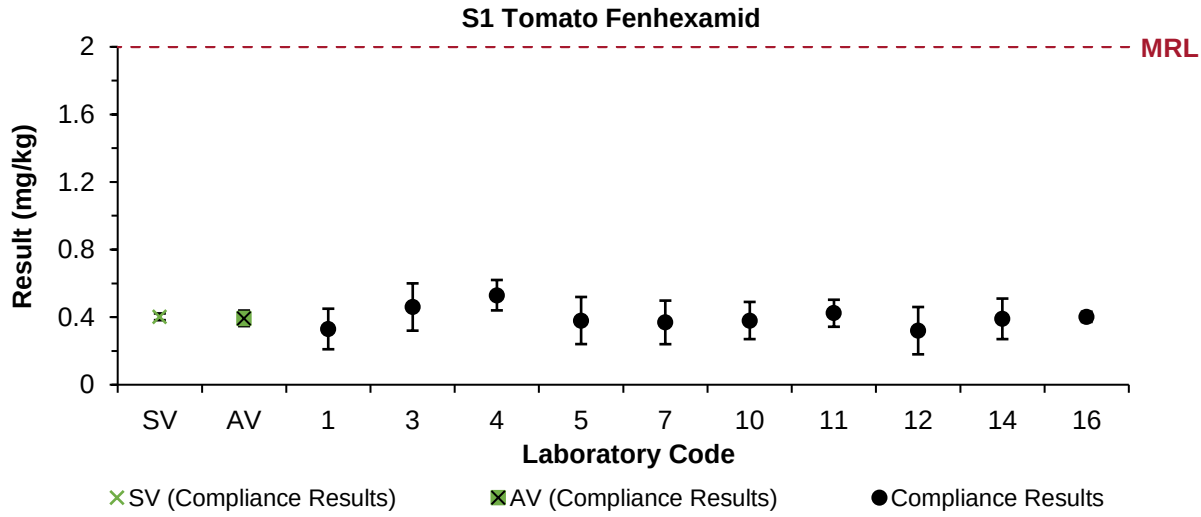

The sample was compliant with the MRL, therefore participants with non-compliance results are in breach.

Figure 20 Sample S1 Tomato Azoxystrobin Spiked and Assigned Value, Results and MRL



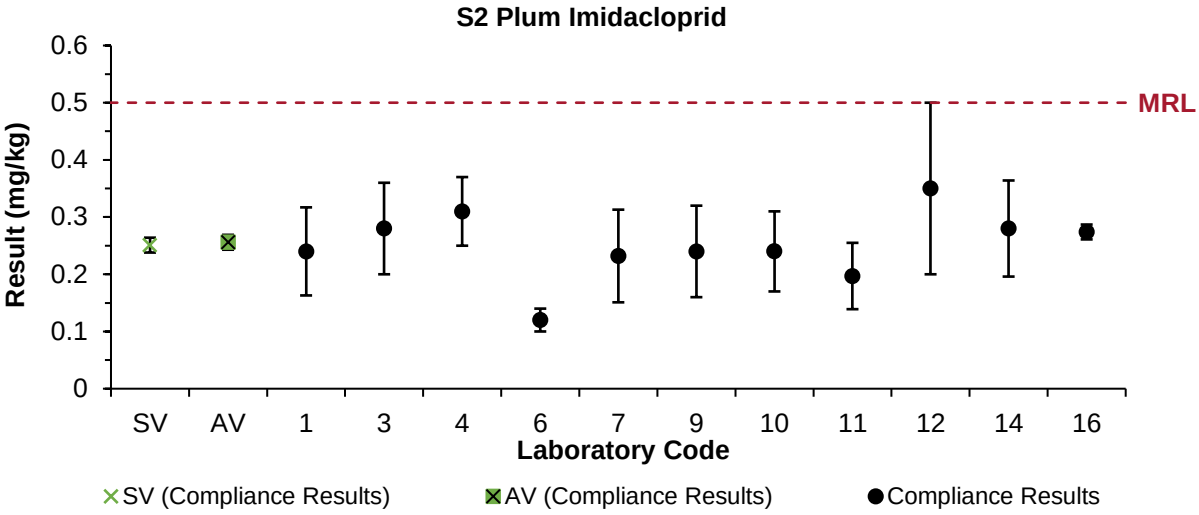

The sample was not compliant with the MRL, therefore participants with compliance results are in breach.

Figure 21 Sample S1 Tomato Chlorpyrifos Spiked and Assigned Value, Results and MRL



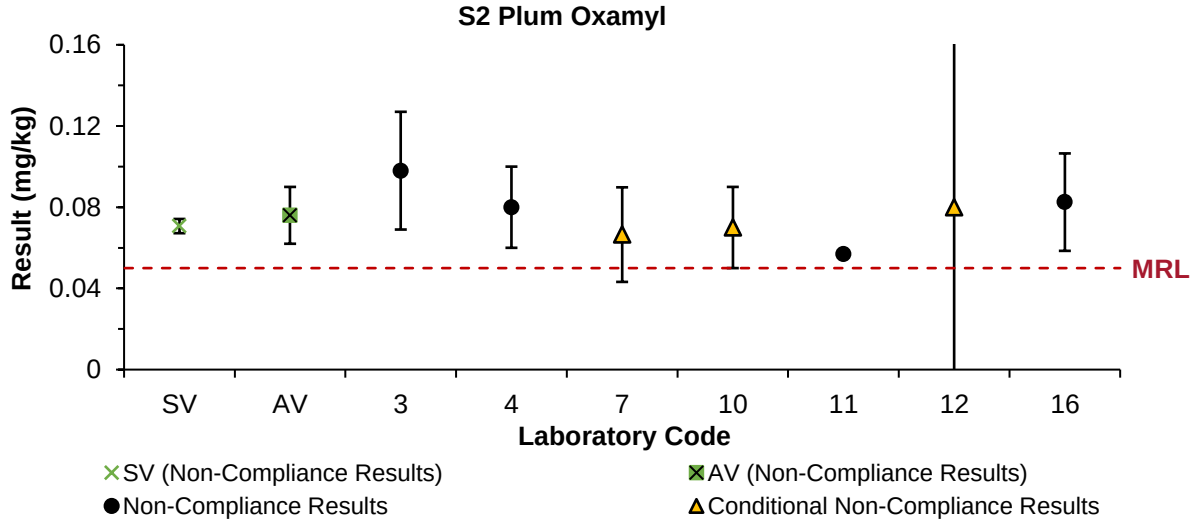

The sample was compliant with the MRL, therefore participants with non-compliance results are in breach.

Figure 22 Sample S1 Tomato Fenhexamid Spiked and Assigned Value, Results and MRL



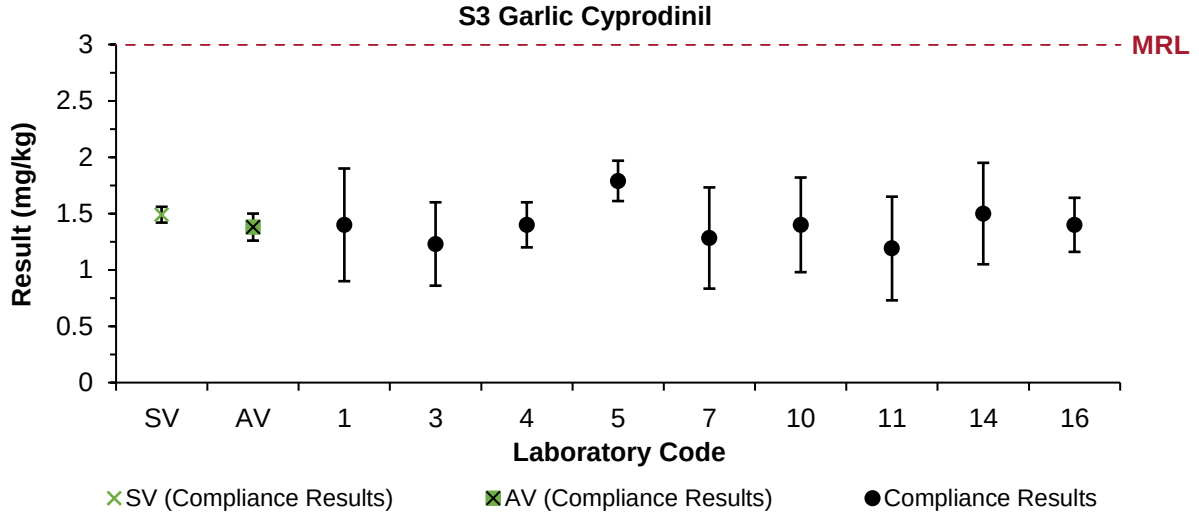

The sample was compliant with the MRL, therefore participants with non-compliance results are in breach.

Figure 23 Sample S2 Plum Imidacloprid Spiked and Assigned Value, Results and MRL




The sample was non-compliant with the MRL, therefore participants with compliance results are in breach.

Figure 24 Sample S2 Plum Oxamyl Spiked and Assigned Value, Results and MRL




The sample was compliant with the MRL, therefore participants with non-compliance results are in breach.

Figure 25 Sample S3 Garlic Cyprodinil Spiked and Assigned Value, Results and MRL

For Sample S1 difenoconazole, and Sample S2 deltamethrin and difenoconazole, the spiked and assigned values were close to and/or spanned the relevant MRL. The results for these analytes are presented in Figures 26 to 28 for information.

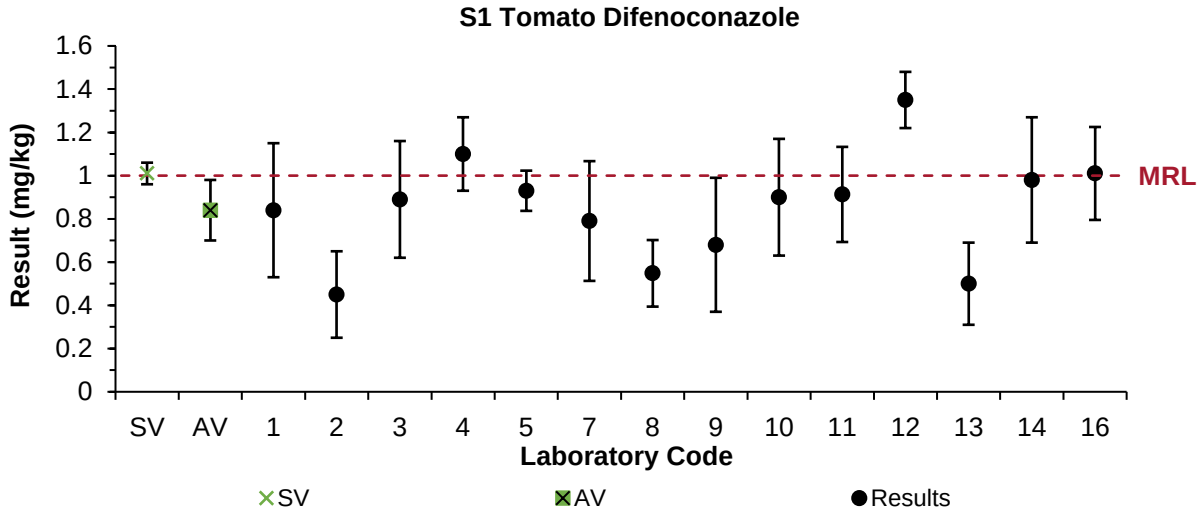



Figure 26 Sample S1 Tomato Difenoconazole Spiked and Assigned Value, Results and MRL

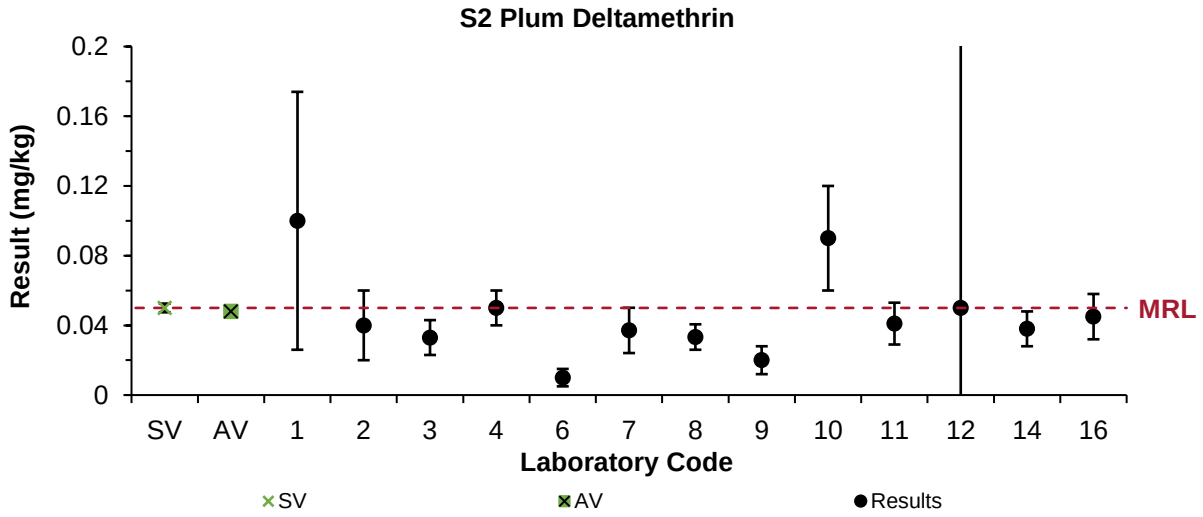



Figure 27 Sample S2 Plum Deltamethrin Spiked and Assigned Value, Results and MRL

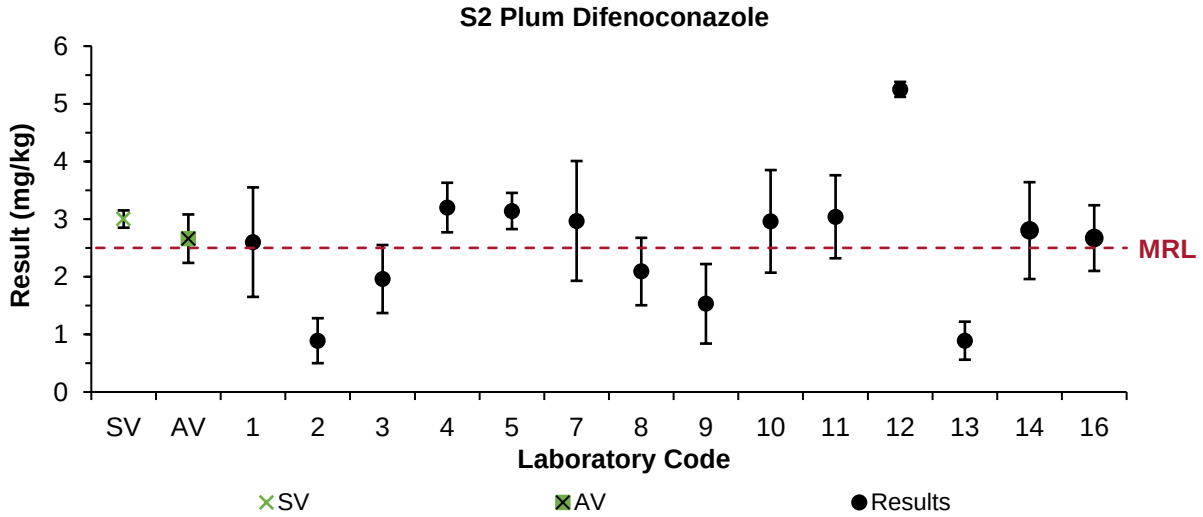



Figure 28 Sample S2 Plum Difenoconazole Spiked and Assigned Value, Results and MRL

### 6.8 Participants' Analytical Methods

A variety of analytical methods were used by participants in this study (Appendix 4).

Results from Laboratory **13** have been removed from all discussion in this section (see also Section 4.2).

Figure 29 shows *z*-scores compared to the sample masses used for analysis. One participant reported using 2.5 g for maleic hydrazide analysis (which has not been included in the below chart as this analyte was not scored), while all other reported sample sizes ranged from 5 g and 20 g per analysis. Most participants reported using 10 g. There was no significant trend observed between results obtained and sample mass used.

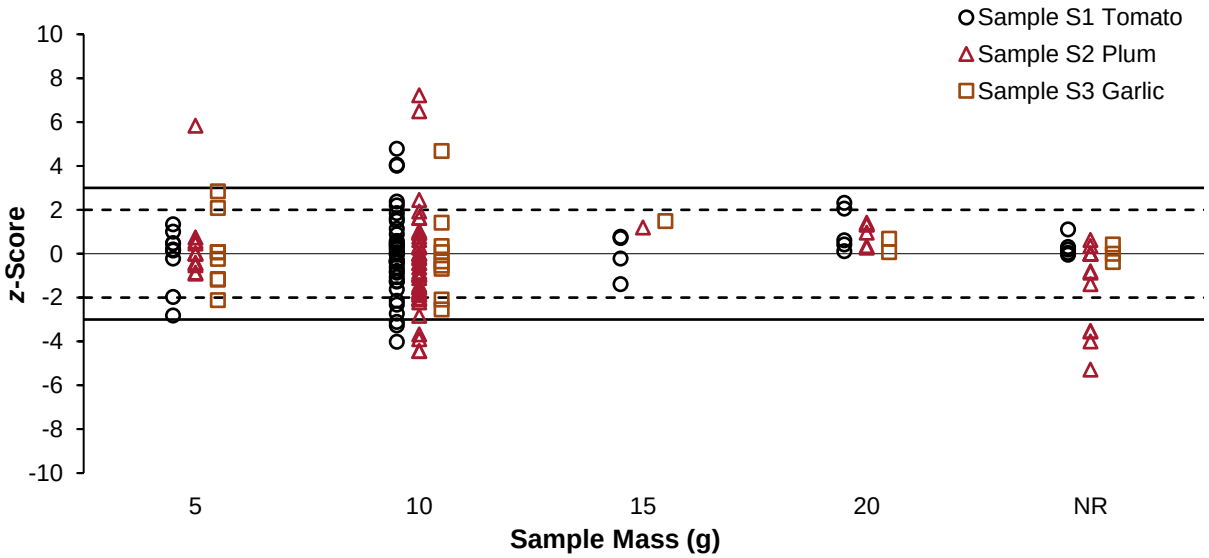



Figure 29 *z*-Score vs Sample Mass Used for Analysis

Participants reported using a variety of extraction techniques including solid-liquid extraction (SLE), QuEChERS or other solid phase extractions (SPE). Extraction solvents used included acetonitrile (ACN) and dichloromethane (DCM). Most participants used a clean-up step for analysis, with the use of PSA, C18, $MgSO_4$, carbon (e.g. Envicarb, GCB), PFTE, and silica gel (e.g. Florisil) being reported. Participants reported using gas chromatography (GC) coupled with mass spectrometry (MS), tandem mass spectrometry (MS/MS), electron capture detection (ECD), flame photometric detection (FPD), or liquid chromatography (LC) coupled with MS/MS.

Results compared to methodology used for all scored analytes are presented in Figures 30 to 42; participant's results yielding unacceptable *z*-scores ($|z| \geq 3.0$) have been circled for reference. Participants used a wide variety of methodologies, and there was no significant trend observed between results obtained and methodology used. The most common methodology was extraction using the QuEChERS procedure,[13] with ACN as the extraction solvent and using GC-MS/MS or LC-MS/MS for analysis, depending on the analyte.

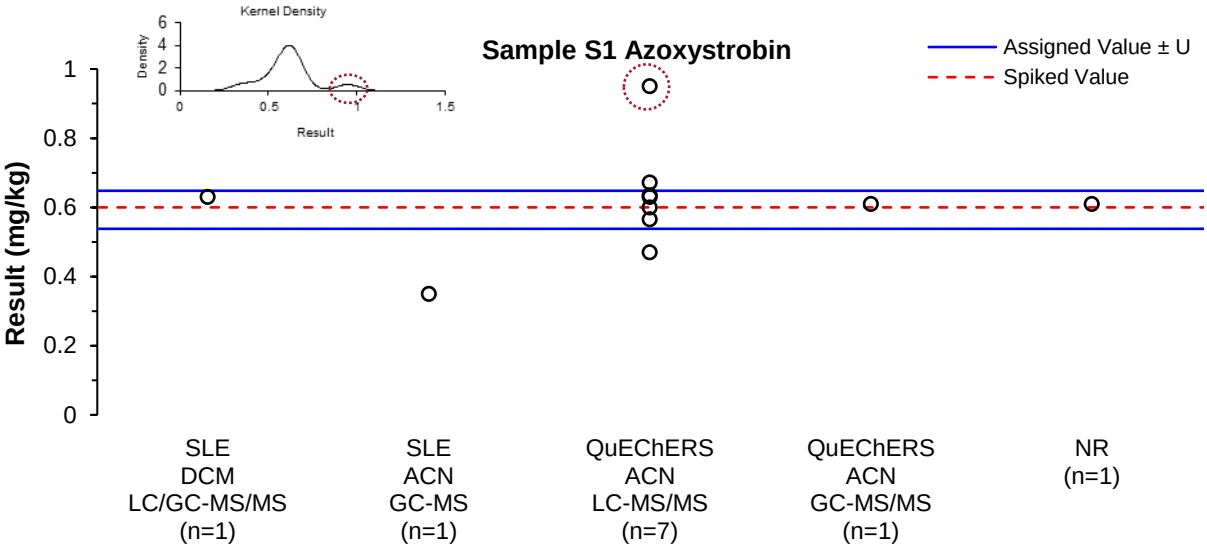



Figure 30 Sample S1 Tomato Azoxystrobin Result vs Methodology

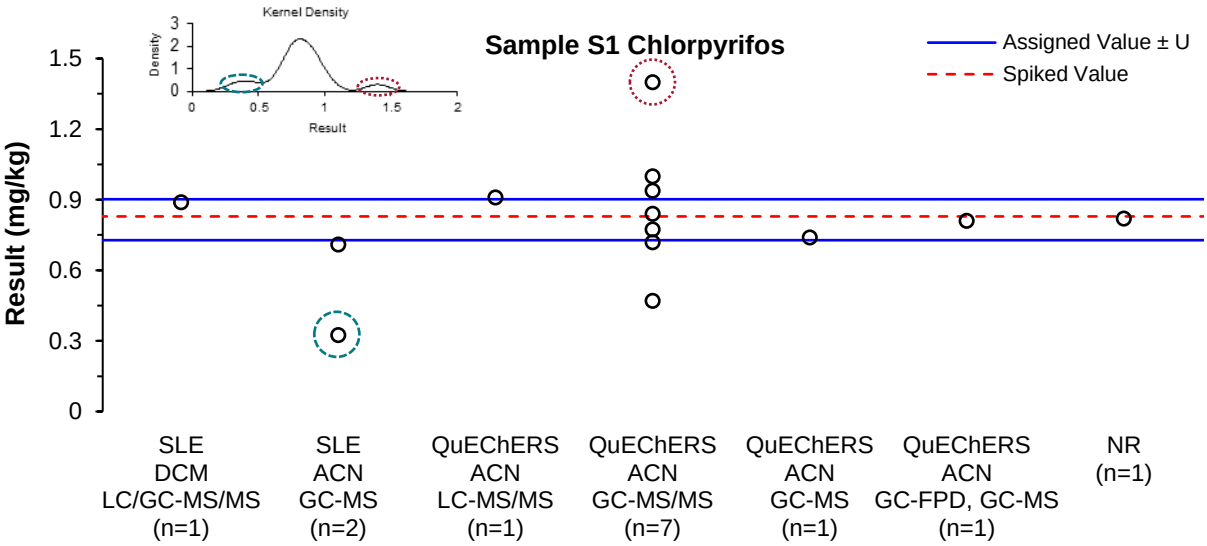



Figure 31 Sample S1 Tomato Chlorpyrifos Result vs Methodology

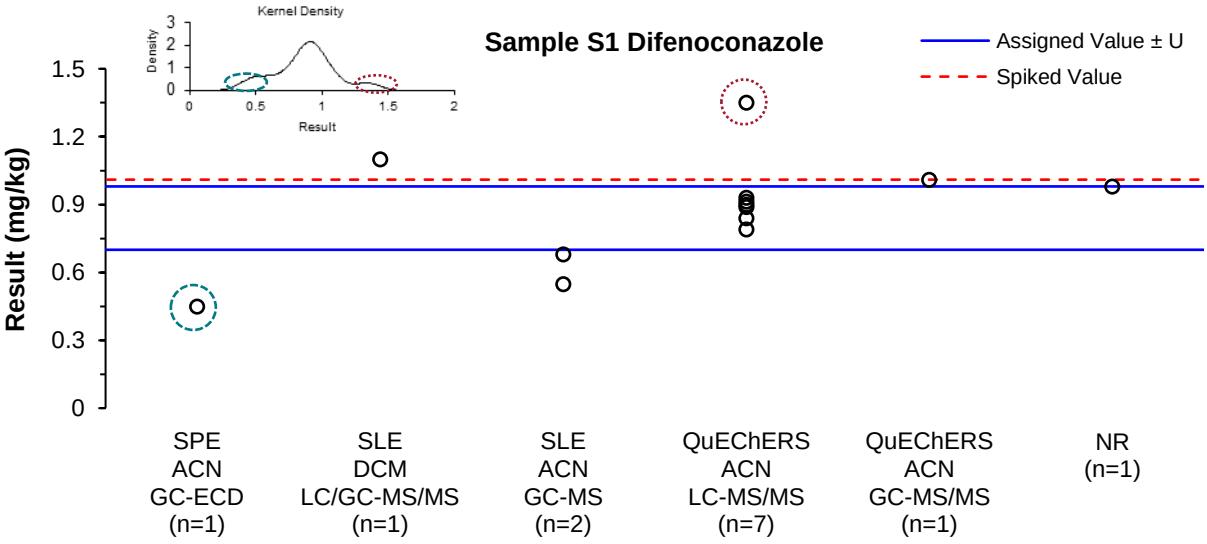



Figure 32 Sample S1 Tomato Difenoconazole Result vs Methodology

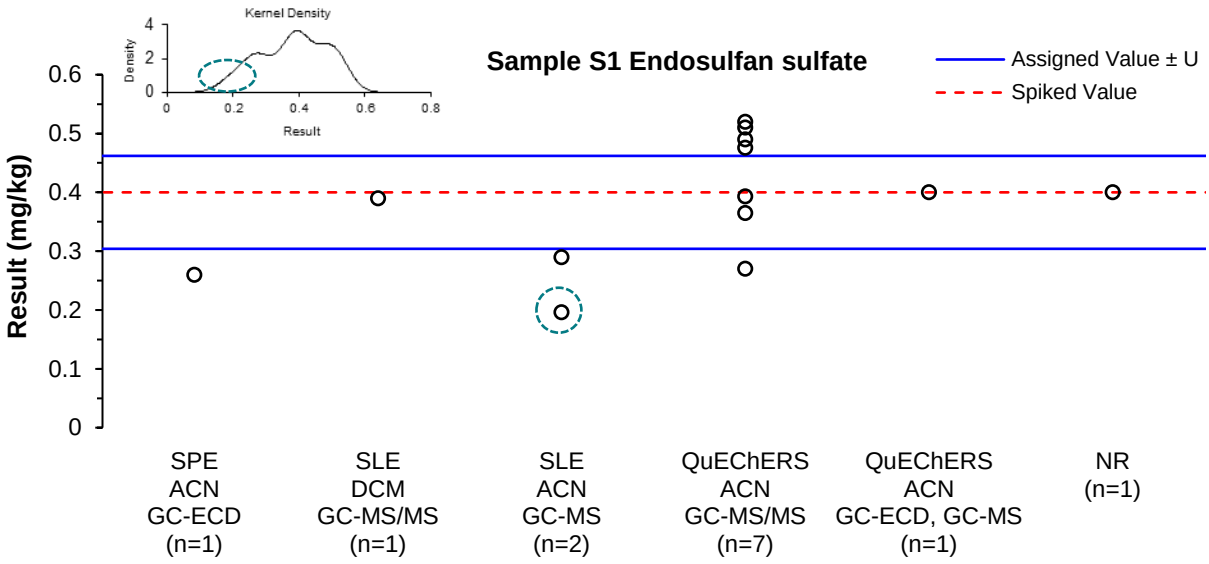



Figure 33 Sample S1 Tomato Endosulfan Sulfate Result vs Methodology

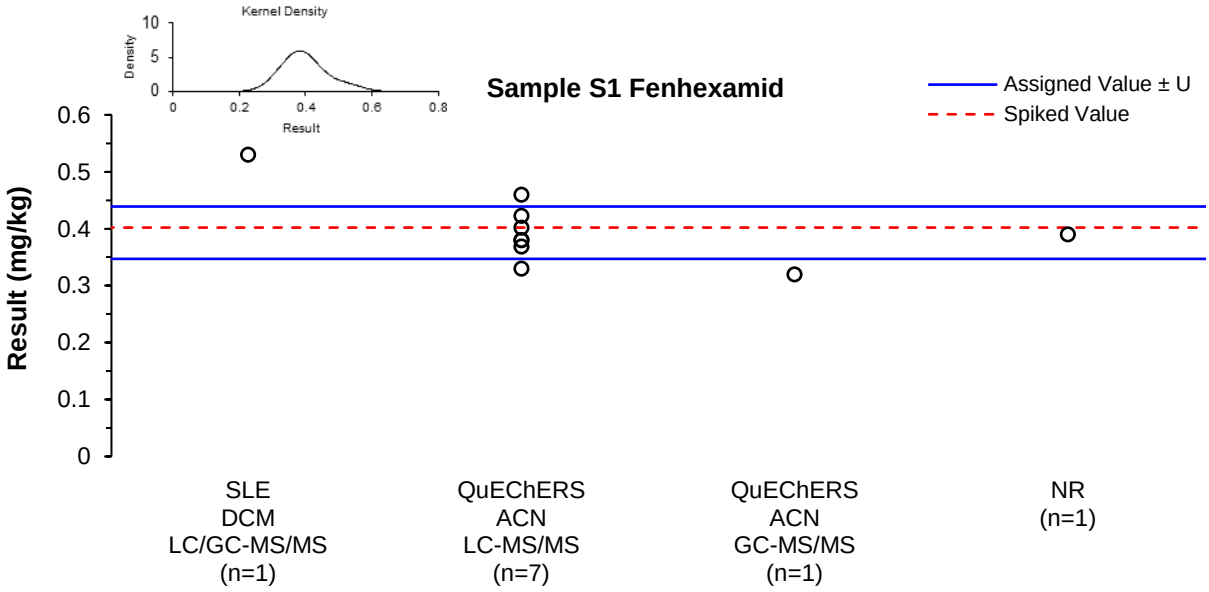



Figure 34 Sample S1 Fenhexamid Result vs Methodology

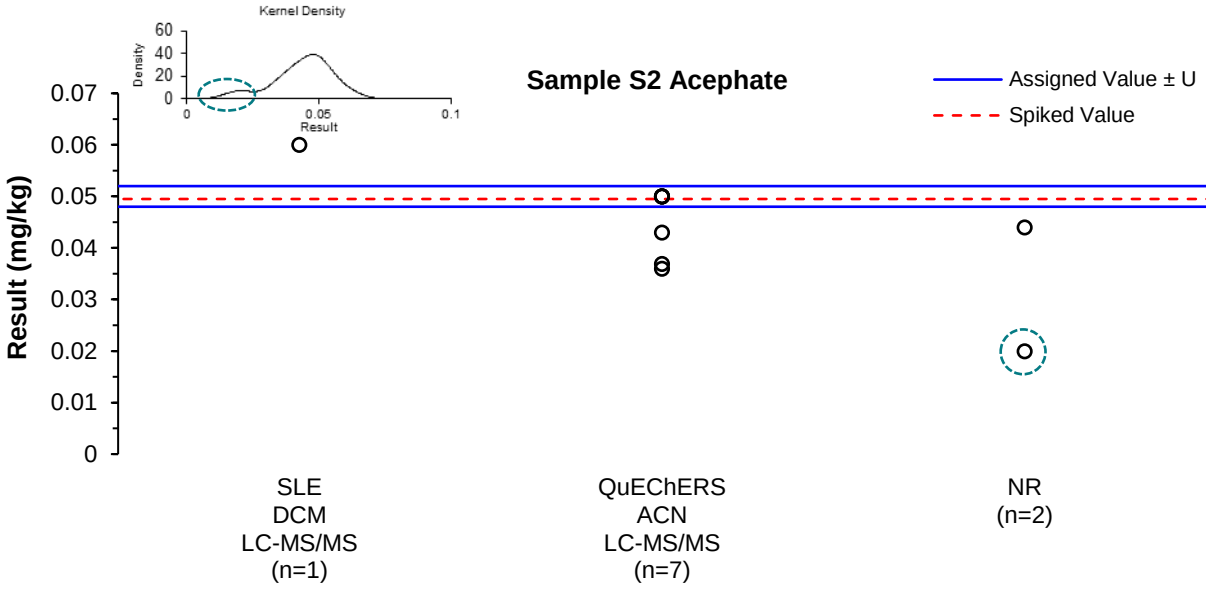



Figure 35 Sample S2 Acephate Result vs Methodology

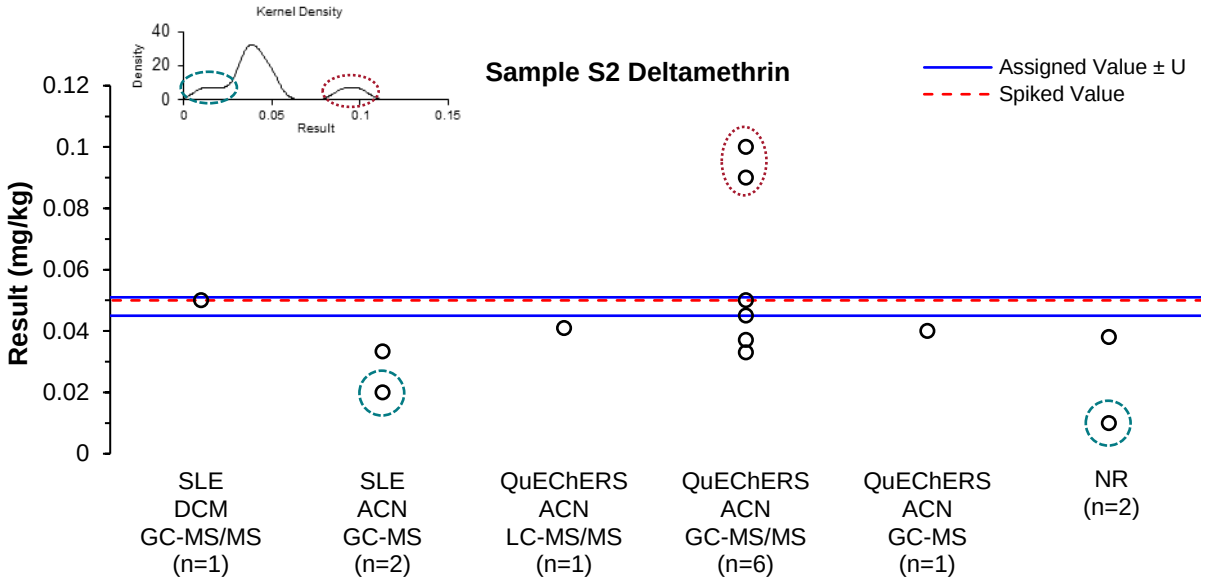



Figure 36 Sample S2 Deltamethrin Result vs Methodology

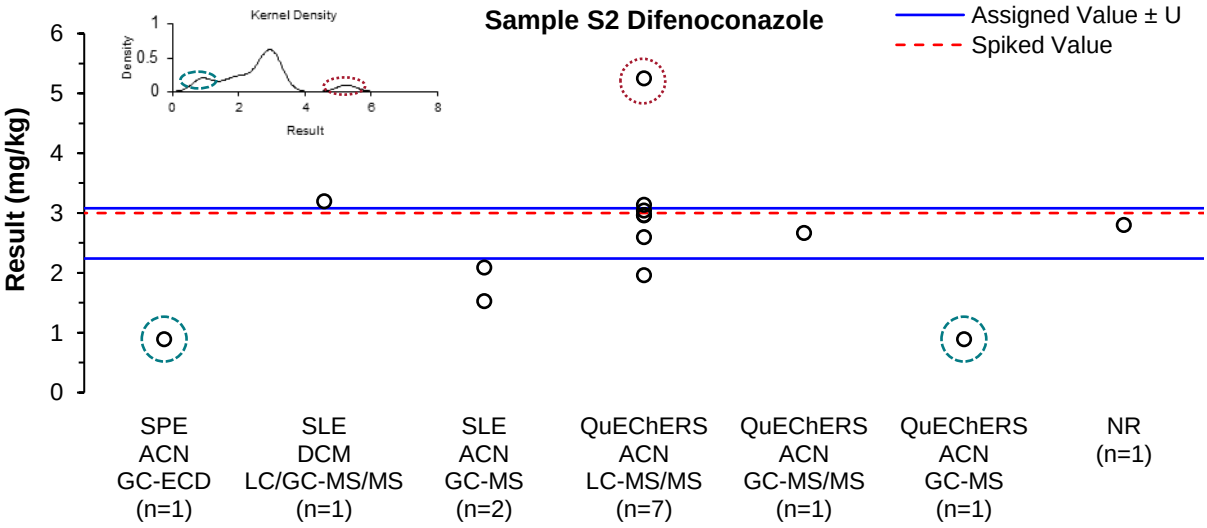



Figure 37 Sample S2 Difenoconazole Result vs Methodology

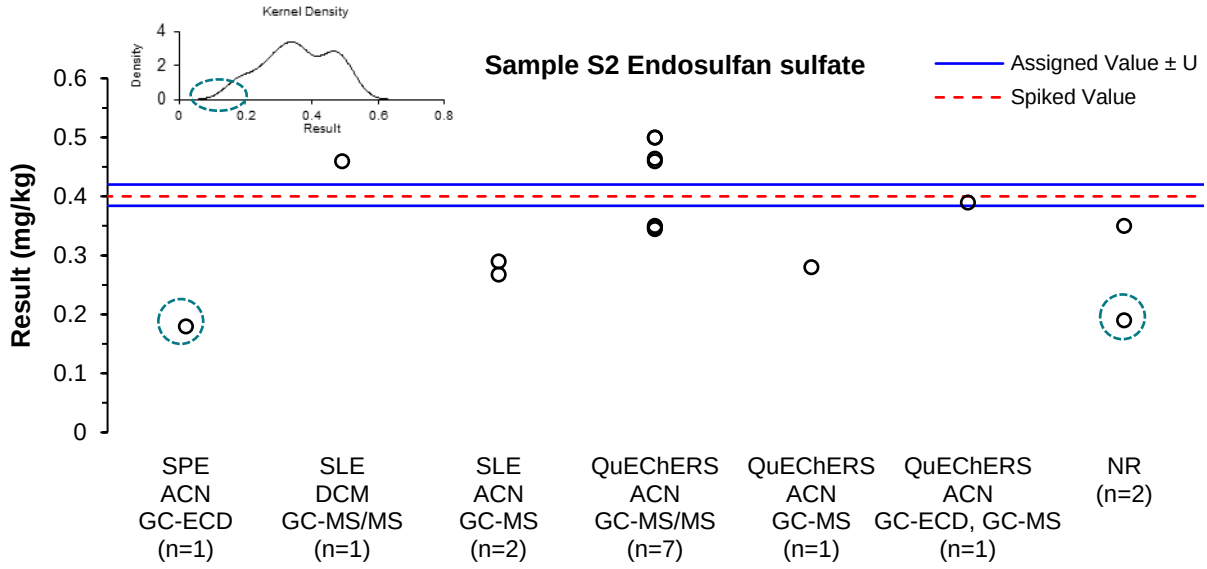



Figure 38 Sample S2 Endosulfan Sulfate Result vs Methodology

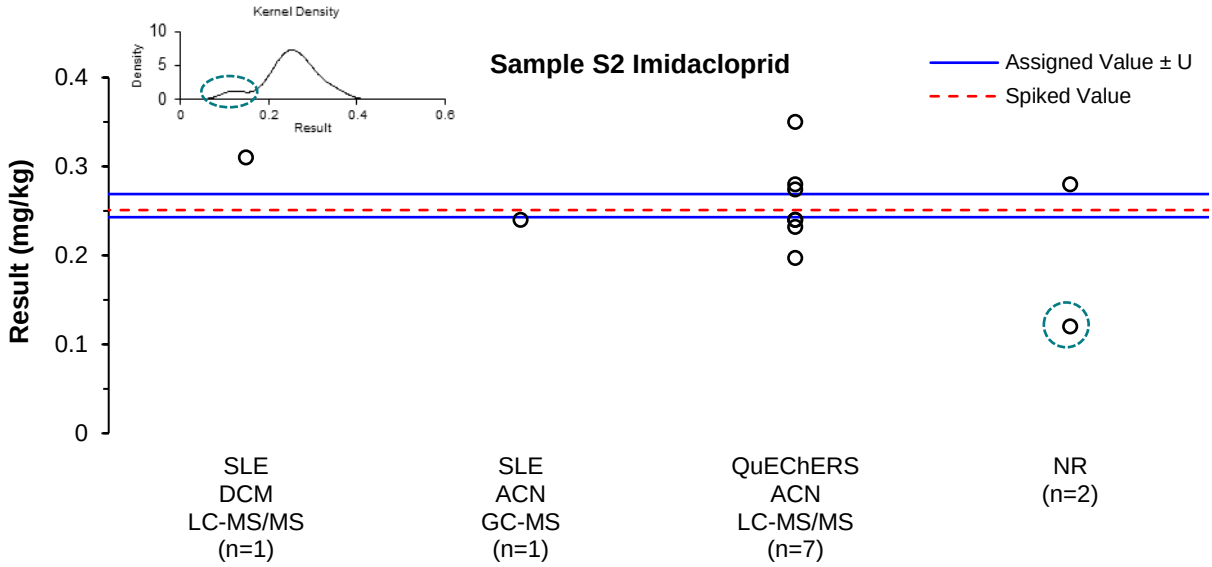



Figure 39 Sample S2 Imidacloprid Result vs Methodology

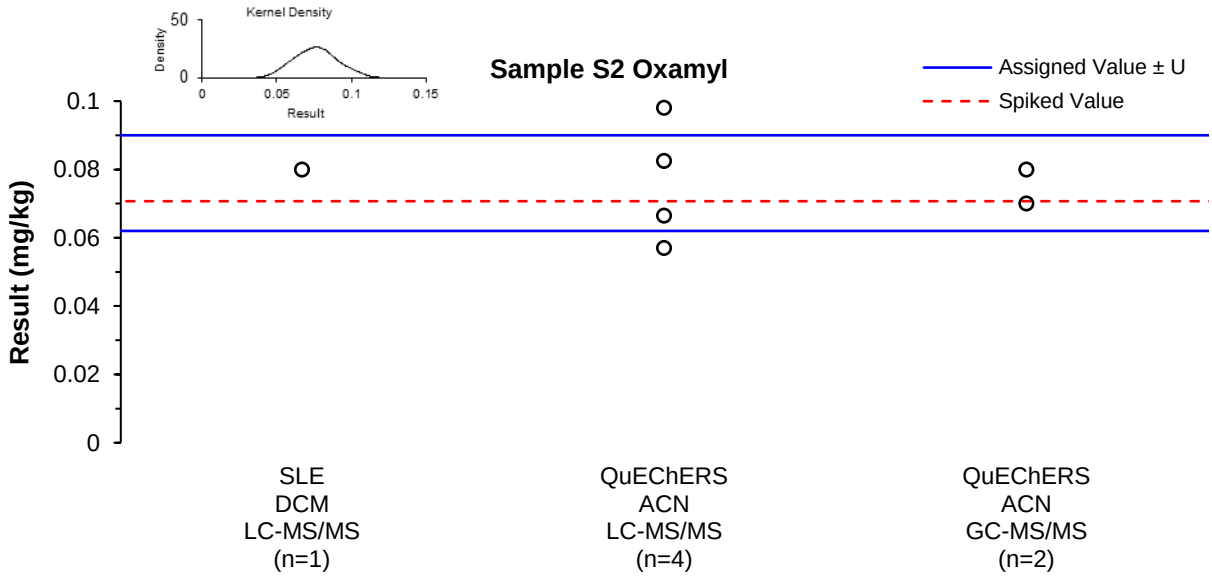



Figure 40 Sample S2 Oxamyl Result vs Methodology

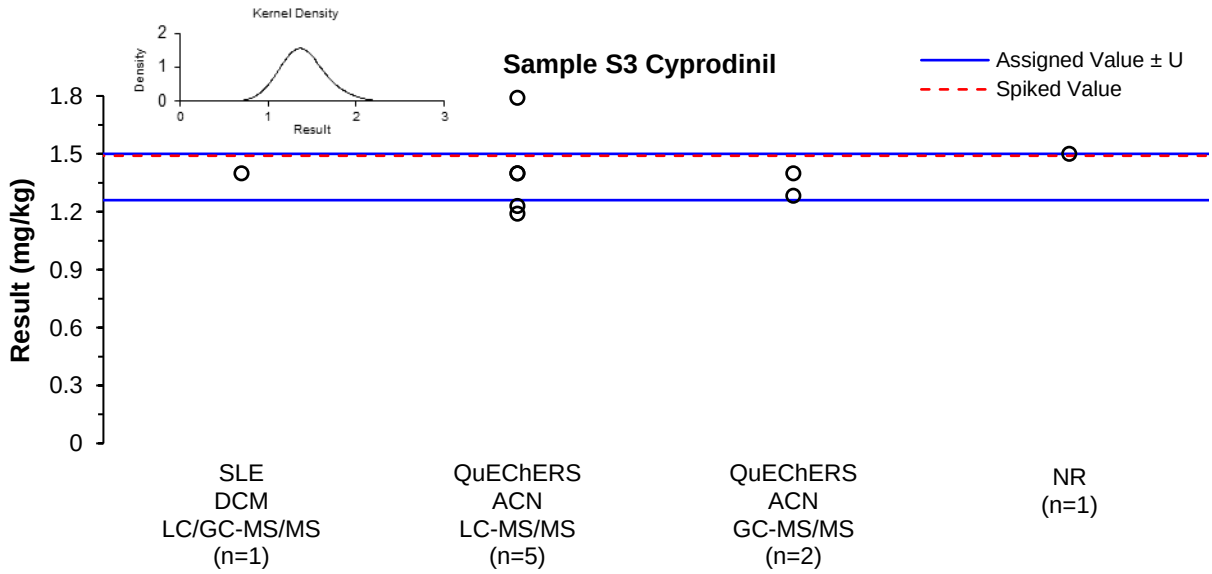



Figure 41 Sample S3 Cyprodinil Result vs Methodology

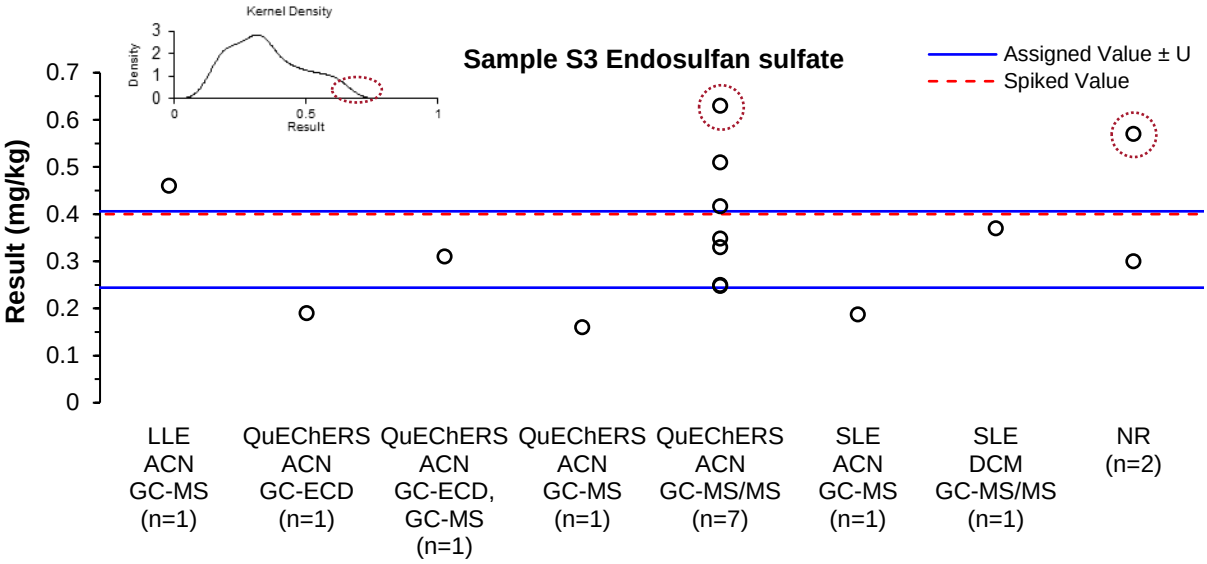



Figure 42 Sample S3 Endosulfan Sulfate Result vs Methodology

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, 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**, **2**, **3**, **4**, **5**, **7**, **8**, **9**, **10**, **11**, **12**, **13**, **14**, **15** and **16** reported recoveries for at least one analyte in this study, and the recoveries reported were within the range of 43% to 125%. Laboratories **1**, **8**, **12**, **14** and **15** reported that they corrected their results for recovery.

Participants were also provided with unspiked samples to be analysed if part of their routine procedures (however were instructed not to correct the spiked sample results for any analytes detected in the unspiked samples). Laboratories **1**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **9**, **10**, **11**, **12**, **14** and **15** reported analysing the unspiked samples.

### 6.9 Certified Reference Materials

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

- AccuStandard
- Dr. Ehrenstorfer
- ISO 17034 certified standards
- Certified standards and compounds from other suppliers

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'*[14]

### 6.10 Effect of Sample Matrix

The samples in this study were purees of tomato (Sample S1), plum (Sample S2) and garlic (Sample S3). A summary of the results reported and acceptable *z*-scores obtained for each matrix is presented in Table 24.

Participants reported the fewest numeric results for analytes in garlic (47% of expected number of results), with significantly more numeric results being reported for tomato (81%) and plum (73%).

The proportion of acceptable *z*-scores returned for each matrix were similar, ranging from 71% to 76%.

Table 24 Result Comparison by Matrix

| Sample | Matrix | Expected Number of Results | Numeric Results Reported | *z*-Scores | Acceptable *z*-Scores |
|---|---|---|---|---|---|
| S1 | Tomato | 80 | 65 (81%) | 65 | 47 (72%) |
| S2 | Plum | 96 | 70 (73%) | 70 | 53 (76%) |
| S3 | Garlic | 64 | 30 (47%) | 24 | 17 (71%) |

Difenoconazole was spiked into both tomato (Sample S1) and plum (Sample S2), at different levels (1.01 mg/kg and 3.00 mg/kg respectively). Participant z-scores for this analyte across both samples are graphed in Figure 43. In general, participants were biased similarly across both matrices. The between-laboratory CV (excluding outliers) for this analyte was also very similar across both matrices (23% and 21% for Samples S1 and S2 respectively).

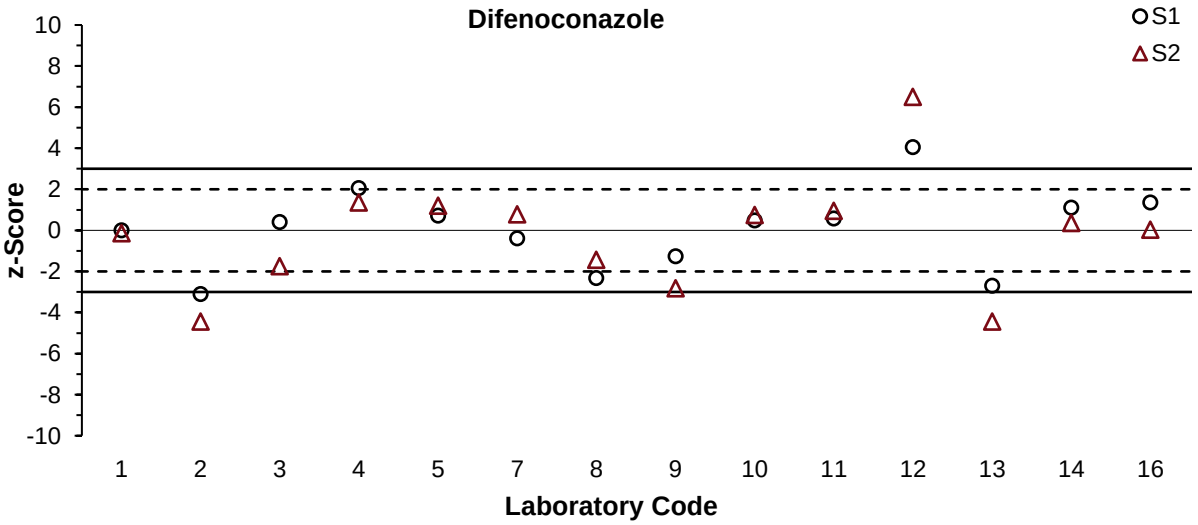



Figure 43 z-Scores for Difenoconazole in Samples S1 and S2

Endosulfan sulfate was spiked into all three matrices, at the same level (0.400 mg/kg). Participant results for this analyte across all samples are graphed in Figure 44. Most participants' results were in agreement with all their other results within their respective uncertainties, except for Laboratory **6** and **16**. The robust average (excluding outliers) to spiked value ratio was the highest for Sample S1 tomato (96%), followed by Sample S2 plum (90%) and then Sample S3 garlic (81%). The between-laboratory CV (excluding outliers) for this analyte was similar across all matrices (30%, 33% and 34% for Samples S1, S2 and S3 respectively).

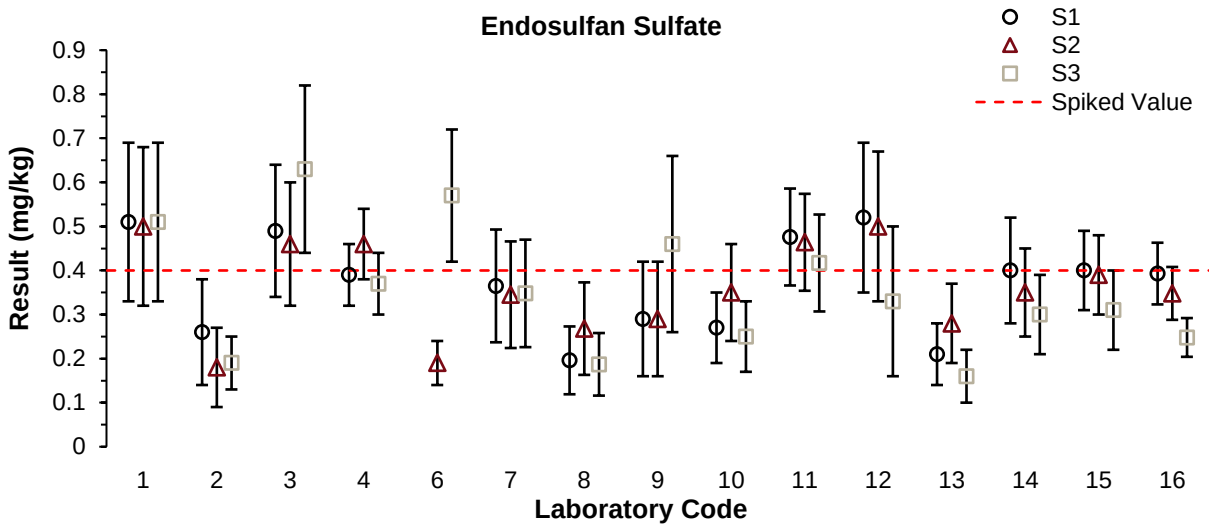



Figure 44 Results for Endosulfan Sulfate in Samples S1, S2 and S3

### 6.11 Summary of Participants' Results and Performances

Summaries of participants' results and performances for scored analytes in this PT study are presented in Tables 25 to 27, and Figure 45.

Table 25 Summary of Participants' Sample S1 Results*

| Lab. Code | Azoxystrobin | Chlorpyrifos | Difenoconazole | Endosulfan sulfate | Fenhexamid |
|---|---|---|---|---|---|
| AV | 0.593 | 0.815 | 0.84 | 0.383 | 0.393 |
| SV | 0.600 | 0.829 | 1.01 | 0.400 | 0.402 |
| 1 | 0.60 | 1.0 | 0.84 | 0.51 | 0.33 |
| 2 | NT | 0.74 | 0.45 | 0.26 | NT |
| 3 | 0.63 | 0.84 | 0.89 | 0.49 | 0.46 |
| 4 | 0.63 | 0.89 | 1.1 | 0.39 | 0.53 |
| 5 | 0.47 | 0.91 | 0.93 | NT | 0.38 |
| 6 | NT | >0.1 | NT | NT | NT |
| 7 | 0.565 | 0.774 | 0.790 | 0.365 | 0.369 |
| 8 | NT | 0.325 | 0.548 | 0.196 | NT |
| 9 | 0.35 | 0.71 | 0.68 | 0.29 | NT |
| 10 | 0.61 | 0.47 | 0.90 | 0.27 | 0.38 |
| 11 | 0.672 | 0.719 | 0.913 | 0.476 | 0.423 |
| 12 | 0.95 | 1.4 | 1.35 | 0.52 | 0.32 |
| 13 | 0.37 | 0.49 | 0.50 | 0.21 | NT |
| 14 | 0.61 | 0.82 | 0.98 | 0.40 | 0.39 |
| 15 | NT | 0.81 | NT | 0.4 | NT |
| 16 | 0.635 | 0.939 | 1.01 | 0.393 | 0.402 |

* All results are mg/kg. Shaded cells are results which returned a questionable or unacceptable *z*-score. AV = Assigned Value; SV = Spiked Value.

Table 26 Summary of Participants' Sample S2 Results*

| Lab. Code | Acephate | Deltamethrin | Difenoconazole | Endosulfan sulfate | Imidacloprid | Oxamyl |
|---|---|---|---|---|---|---|
| AV | 0.050 | 0.048 | 2.66 | 0.402 | 0.256 | 0.076 |
| HV | 0.050 | 0.049 | - | 0.400 | 0.254 | - |
| SV | 0.0495 | 0.05 | 3.00 | 0.400 | 0.251 | 0.0707 |
| 1 | 0.05 | 0.10 | 2.6 | 0.50 | 0.24 | NT |
| 2 | NT | 0.04 | 0.89 | 0.18 | NT | NT |
| 3 | 0.043 | 0.033 | 1.96 | 0.46 | 0.28 | 0.098 |
| 4 | 0.06 | 0.05 | 3.2 | 0.46 | 0.31 | 0.08 |
| 5 | NT | NT | 3.14 | NT | NT | NT |
| 6 | 0.02 | 0.01 | NT | 0.19 | 0.12 | NT |
| 7 | 0.0369 | 0.0371 | 2.968 | 0.345 | 0.232 | 0.0665 |
| 8 | NT | 0.0333 | 2.090 | 0.268 | NT | NT |
| 9 | NT | 0.02 | 1.53 | 0.29 | 0.24 | NT |
| 10 | 0.05 | 0.09 | 2.96 | 0.35 | 0.24 | 0.07 |
| 11 | 0.036 | 0.041 | 3.04 | 0.464 | 0.197 | 0.057 |
| 12 | 0.05 | 0.05 | 5.25 | 0.5 | 0.35 | 0.08 |
| 13 | NT | NR | 0.89 | 0.28 | NT | NT |
| 14 | 0.044 | 0.038 | 2.8 | 0.35 | 0.28 | <0.01 |
| 15 | NT | <0.01 | NT | 0.39 | NT | NT |
| 16 | 0.05 | 0.045 | 2.67 | 0.348 | 0.274 | 0.0825 |

* All results are mg/kg. Shaded cells are results which returned a questionable or unacceptable *z*-score. AV = Assigned Value; HV = Homogeneity Value; SV = Spiked Value.

Table 27 Summary of Participants' Sample S3 Results*

| Lab. Code | Cyprodinil | Endosulfan sulfate |
|---|---|---|
| AV | 1.38 | 0.325 |
| HV | 1.38 | 0.39 |
| SV | 1.49 | 0.400 |
| 1 | 1.4 | 0.51 |
| 2 | NT | 0.19 |
| 3 | 1.23 | 0.63 |
| 4 | 1.4 | 0.37 |
| 5 | 1.79 | NT |
| 6 | <0.01 | 0.57 |
| 7 | 1.283 | 0.348 |
| 8 | NT | 0.187 |
| 9 | NT | 0.46 |
| 10 | 1.40 | 0.25 |

| Lab. Code | Cyprodinil | Endosulfan sulfate |
|---|---|---|
| 11 | 1.19 | 0.417 |
| 12 | NR | 0.33 |
| 13 | NT | 0.16 |
| 14 | 1.5 | 0.30 |
| 15 | NT | 0.31 |
| 16 | 1.4 | 0.248 |

* All results are mg/kg. Shaded cells are results which returned a questionable or unacceptable *z*-score. AV = Assigned Value; HV = Homogeneity Value; SV = Spiked Value.

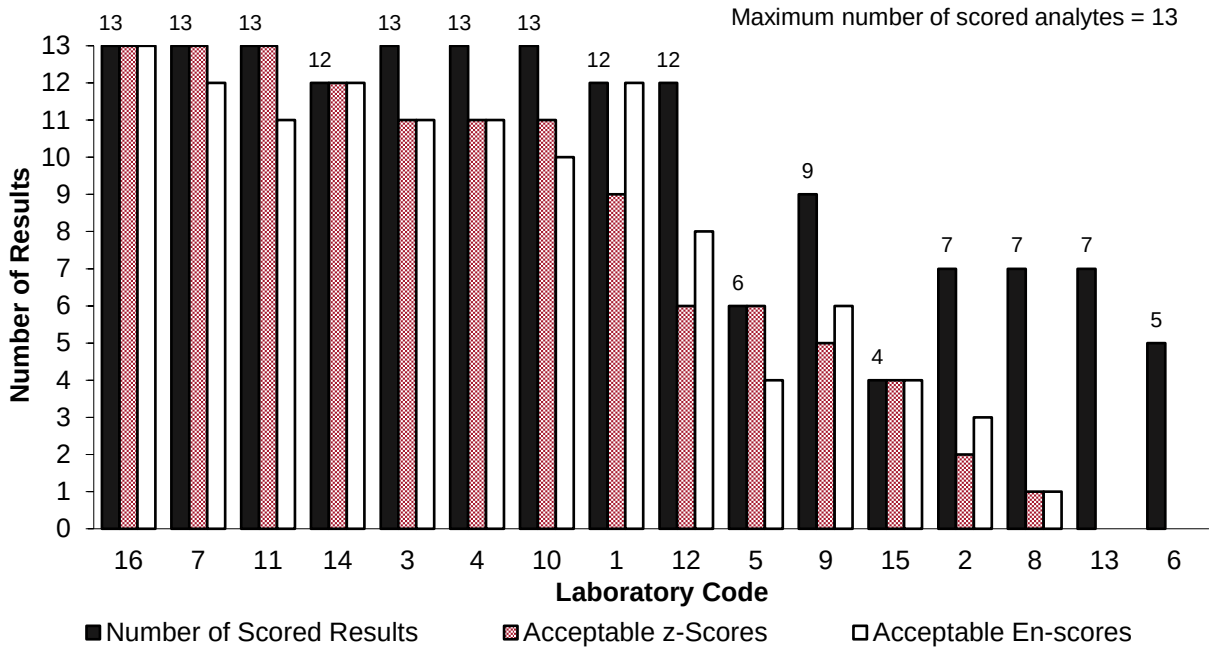



Figure 45 Summary of Participants' Performance

### 6.12 Comparison with Previous Pesticides in Fruit and Vegetables PT Studies

A summary of participation and reported results rates in NMI Pesticides in Fruit and Vegetables PT studies over the last 10 studies (2016 to 2024) is presented in Figure 46. The numeric results reported by participants have remained steady over this period.

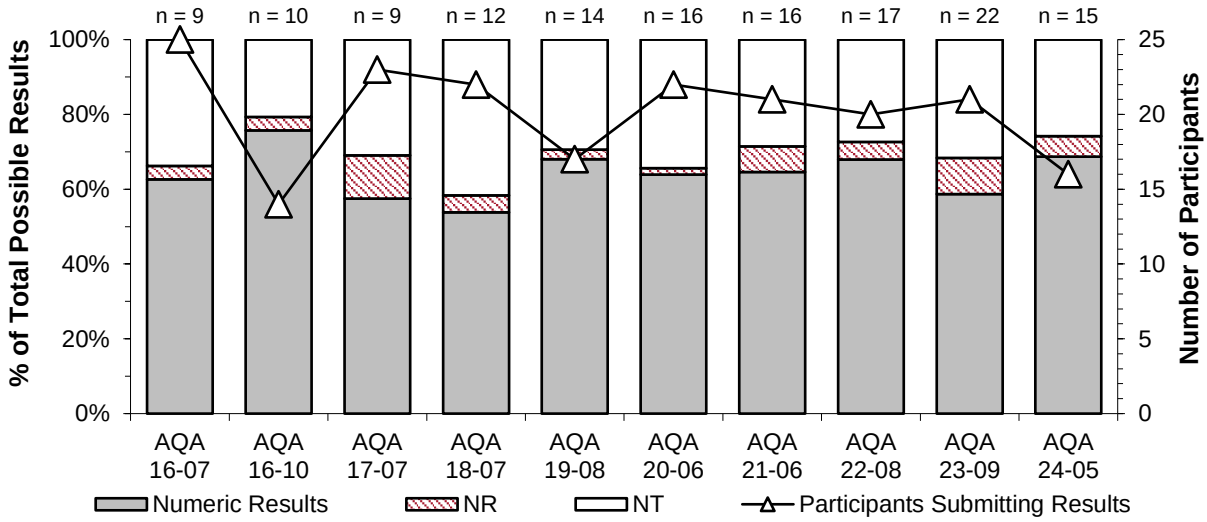



Figure 46 Summary of Participation and Reported Results in NMI Pesticides in Fruit and Vegetables PT Studies (n = number of included analytes)

A summary of the acceptable performance (presented as a percentage of the total number of scores for each study) in NMI Pesticides in Fruit and Vegetables PT studies over the last 10 studies (2016 to 2024) is presented in Figure 47. Over this period, the proportion of acceptable *z*-scores and $E_n$-scores has remained steady, with the average being 77% and 71% for $E_n$-scores.

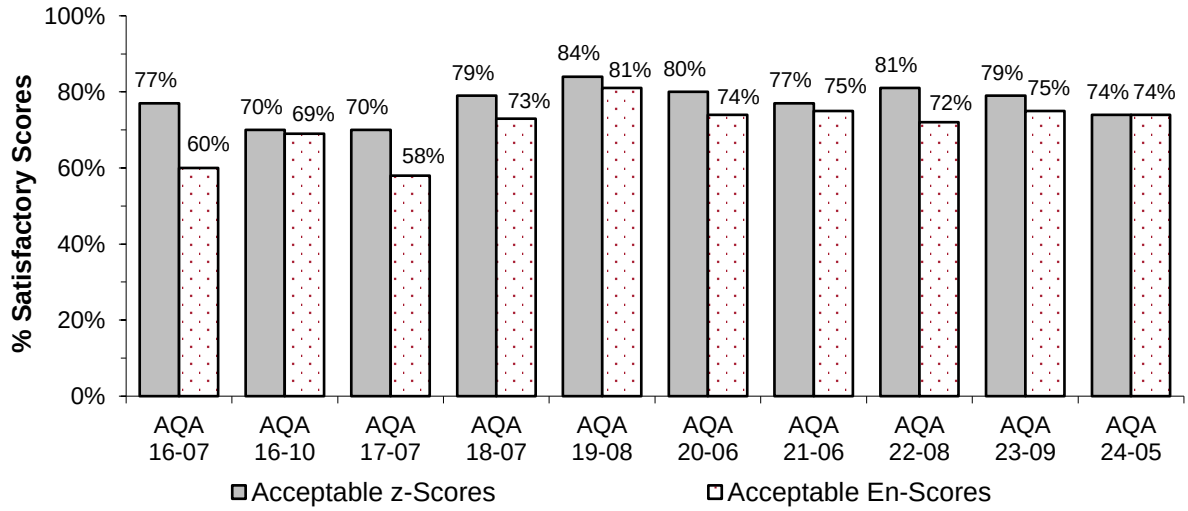



Figure 47 Summary of Participants' Performance in NMI Pesticides in Fruit and Vegetables PT Studies

Individual performance history reports are also 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 method or laboratory bias.

As discussed in Section 0, it is a requirement of ISO/IEC 17025 that laboratories report their uncertainties.[9] Figure 48 presents a summary of the relative uncertainties as reported by participants over the last 10 studies (2016 – 2024). Over this time period, most numeric results were reported with uncertainties (86%), with on average 67% of participants in each

study reporting that they were accredited to ISO/IEC 17025. Most participants over this time period reported relative expanded uncertainties between 15% and 50%, however around 37% of relative uncertainties were outside this range and may have been unrealistically small or too large and not fit-for-purpose. This proportion has been decreasing (improving) over the last few studies.

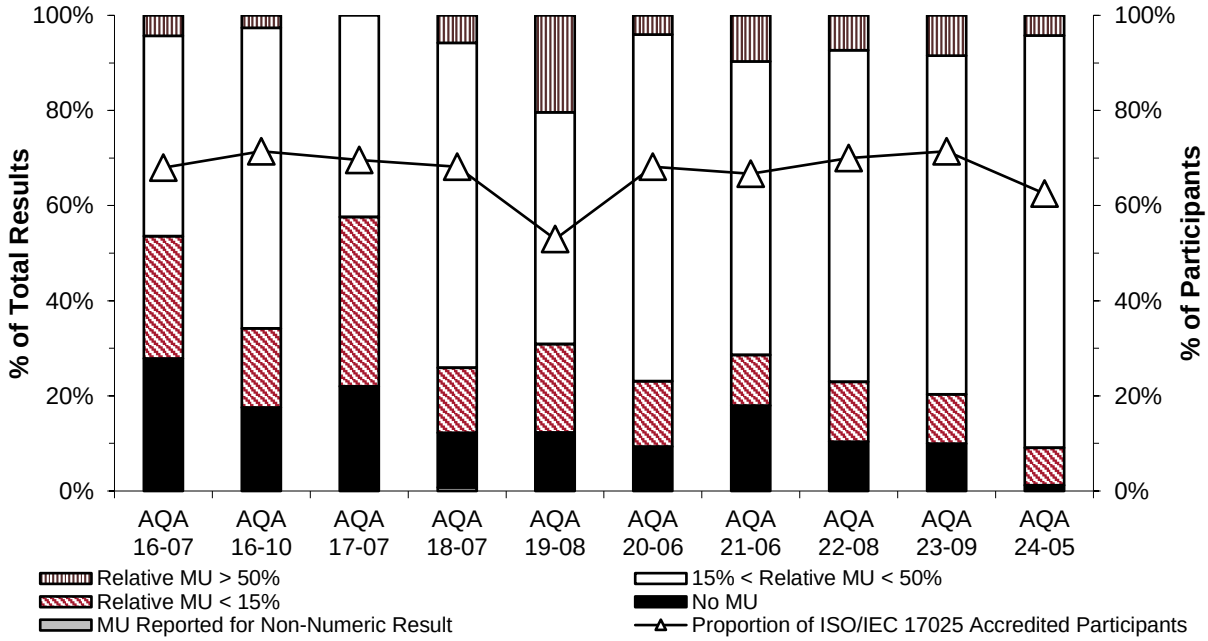



Figure 48 Summary of Participant' Relative Uncertainties for NMI Pesticides in Fruit and Vegetables PT Studies

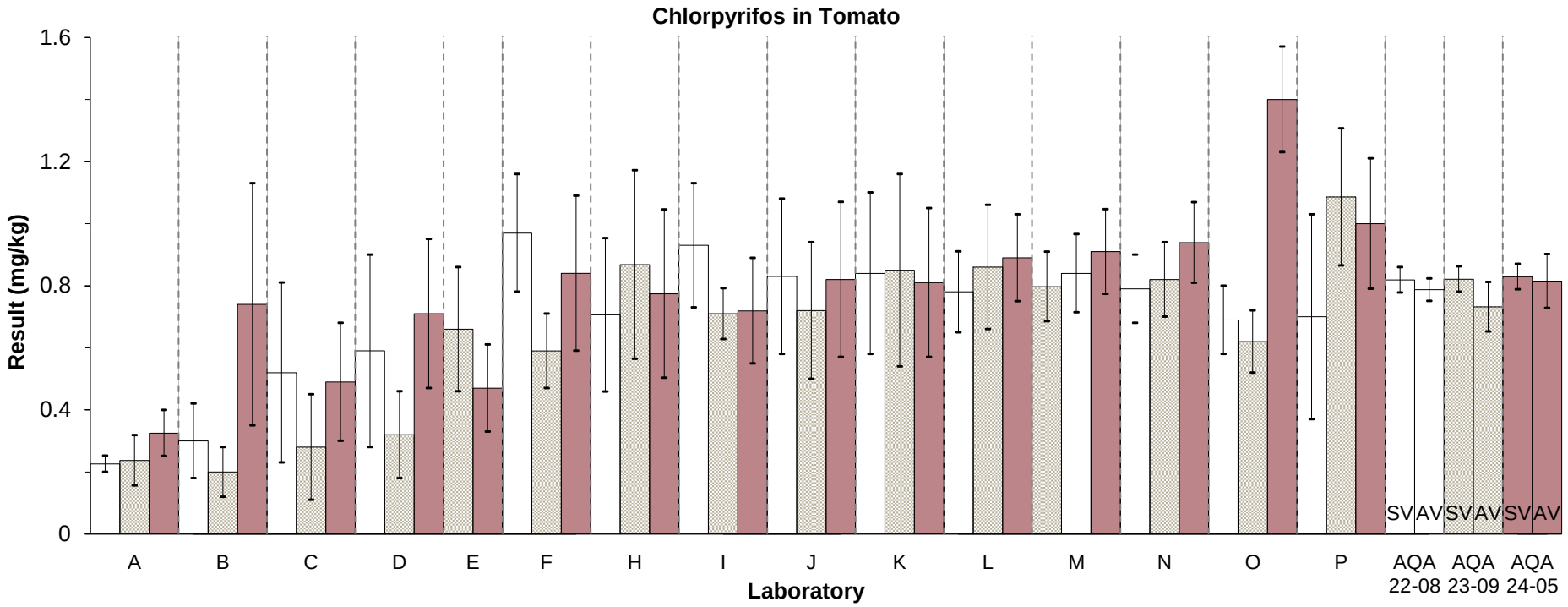
**Chlorpyrifos in Tomato**

For this study, chlorpyrifos was spiked into Sample S1 (tomato) at a similar level as for previous PT studies AQA 23-09 Sample S1 and AQA 22-08 Sample S1 (both also tomato).

Participants' results for chlorpyrifos in tomato over these three studies are shown in Figure 49, for participants who reported results in this and at least one previous study. Most participants reported similar results across all studies, however there were some participants whose results were not in agreement with each other across all three studies within their reported expanded uncertainties: Laboratories B, D, F and O (in Figure 49).

In all studies, the assigned values and the spiked values were in agreement with each other within their respective expanded uncertainties.

In this year's study, variability of participants' results was lower as compared to the previous two studies, and the ratio of the assigned value to spiked value was higher compared to the previous two studies, reflecting an improvement in the analysis of chlorpyrifos in tomato.




SV = Spiked Value; AV = Assigned Value.

Figure 49 AQA 22-08, AQA 23-09 and AQA 24-05 Chlorpyrifos in Tomato Results

## 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] NMI, 2024, *Study Protocol for Proficiency Testing*, viewed October 2024, <https://www.industry.gov.au/sites/default/files/2020-10/cpt_study_protocol.pdf>.

[3] NMI, 2024, *Chemical Proficiency Testing Statistical Manual*, viewed October 2024, <https://www.industry.gov.au/sites/default/files/2019-07/cpt_statistical_manual.pdf>.

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

[5] Federal Register of Legislation, 2024, *Australia New Zealand Food Standards Code – Schedule 20 – Maximum residue limits*, viewed July 2024, <https://www.legislation.gov.au/F2015L00468/latest/text>.

[6] Food and Agriculture Organization of the United Nations, *NSP - List of Pesticides evaluated by JMPS and JMPR*, viewed October 2024, <https://www.fao.org/agriculture/crops/thematic-sitemap/theme/pests/lpe/en/>.

[7] ISO 13528, *Statistical methods for use in proficiency testing by interlaboratory comparison*.

[8] 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.

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

[10] Eurachem/CITAC Guide CG 4, QUAM:2012.P1, *Quantifying Uncertainty in Analytical Measurement*, 3rd edition, viewed October 2024, <http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf>.

[11] ISO/IEC Guide 98-3:2008, *Uncertainty of measurement – Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*.

[12] NATA, 2020, *Update to Measurement Uncertainty resources*, viewed October 2024, <https://nata.com.au/news/update-to-measurement-uncertainty-resources/>

[13] Anastassiades, M., Lehotay, S.J., Štajnbaher, D. and Schenck, F.J., 2003, 'Fast and Easy Multiresidue Method Employing Acetonitrile Extraction/Partitioning and "Dispersive Solid-Phase Extraction" for the Determination of Pesticide Residues in Produce', *J. AOAC Int*., vol. 86, pp. 412-431.

[14] BIPM, JCGM 200:2012, *International vocabulary of metrology – Basic and general concepts and associated terms (VIM)*, 3rd edition, viewed October 2024, <https://www.bipm.org/utils/common/documents/jcgm/JCGM_200_2012.pdf>.

[15] Federal Register of Legislation, 2024, *Australia New Zealand Food Standards Code – Schedule 22 – Foods and classes of foods*, viewed July 2024, <https://www.legislation.gov.au/F2015L00433/latest/text>.

[16] Fearn, T. and Thompson, M., 2001, ‘A new test for ‘sufficient homogeneity’’, *Analyst*, vol. 126, pp. 1414-1417.

## APPENDIX 1 SAMPLE PREPARATION

Tomatoes and plums were bought from a local organic fruit and vegetable wholesaler. Garlic was bought from a local grocery store. The portion of fruit and vegetables prepared was in accordance with the Australian New Zealand Food Standards Code – Schedule 22 – Foods and classes of foods.[15]

### Preparation of Sample S1 (Tomato)

The tomatoes were rinsed using tap water and allowed to air dry. The tomatoes, including the peel, were pureed and passed through an 850 µm sieve. The sieved puree was continuously stirred while aliquots of at least 100 g were dispensed into 200 mL amber bottles to provide unspiked samples. The remaining puree was spiked with pesticide standard solutions. The spiked puree was stirred for at least two hours before aliquots of at least 100 g were dispensed into 200 mL amber bottles to provide spiked samples. Each bottle was then labelled, shrink-wrapped and placed in a freezer.

### Preparation of Sample S2 (Plum)

The plums were rinsed with tap water, and the stones were removed. The remainder was then pureed and passed through an 850 µm sieve. The sieved puree was continuously stirred while aliquots of at least 100 g were dispensed into 200 mL amber bottles to provide unspiked samples. The remaining puree was spiked with pesticide standard solutions. The spiked puree was stirred for at least two hours before aliquots of at least 100 g were dispensed into 200 mL amber bottles to provide spiked samples. Each bottle was then labelled, shrink-wrapped and placed in a freezer.

### Preparation of Sample S3 (Garlic)

The garlic cloves were pureed. Water was added to help facilitate passing the puree through an 850 µm sieve. The sieved puree was continuously stirred while aliquots of at least 50 g were dispensed into 100 mL amber bottles to provide unspiked samples. The remaining puree was spiked with pesticide standard solutions. The spiked puree was stirred for at least 2 hours before aliquots of at least 50 g were dispensed into 100 mL amber bottles to provide spiked samples. Each bottle was then labelled, shrink-wrapped and placed in a freezer.

## APPENDIX 2 REFERENCE VALUES, HOMOGENEITY AND STABILITY

### A2.1 Reference Values

**Sample S2 Reference Values**

Reference values were obtained for Sample S2 acephate, deltamethrin, endosulfan sulfate and imidacloprid. Analysis for the provision of these reference values was done by NMI Chemical Reference Values.

The samples were analysed by isotope-dilution mass spectrometry (IDMS). A mixed internal standard solution with mass fractions matched to the sample was prepared from deuterium-labelled analogues of all pesticides. Blends were prepared gravimetrically by adding a single aliquot of mixed internal standard solution to 10 g of sample. Matched calibration blends were prepared using the mixed internal standard and aliquots of a gravimetrically prepared standard solution containing the four pesticide reference materials. Pesticides were extracted from samples using acidified acetonitrile, magnesium sulfate and sodium acetate following the QuEChERS methodology. Extracts were subjected to dispersive solid-phase extraction (dSPE) with PSA/C18EC/$MgSO_4$ (C18) cartridges. Diluted dSPE extracts were analysed using two-dimensional liquid chromatography tandem mass spectrometry (2D LC-MS/MS) on a Sciex Exion 2DLC and Sciex 7500 MS. Undiluted dSPE extracts were analysed using a liquid chromatography quadrupole time-of-flight mass spectrometry (LC-QTOF) method on a Sciex Exion LC with Sciex 7600 QTOF.

Samples for reference value assignment were analysed in multiple batches. All samples were extracted in duplicate or more and were analysed by both the 2D LC-MS/MS and LC-QTOF methods. Results from both methods were used for reference value setting and results from the 2D LC-MS/MS method were used for statistical assessment of homogeneity.

Standard uncertainties were estimated and combined as described in the JCGM Guide to the Expression of Uncertainty in Measurement (ISO GUM).[11] Contributions to the standard measurement uncertainty were the preparation of calibration standards, gravimetric mass measurements, method precision, between-bottle homogeneity, ion peak area ratios (Rx, Ry and Rz) and potential biases (matrix interferences within and between methods, batch-to-batch variability). The combined standard uncertainties were expanded to a level of confidence of 95% using a coverage factor calculated from the effective degrees of freedom obtained from the Welch-Satterthwaite equation.

The reference values obtained for the Sample S2 analytes are presented in Table 28. The reference values for these Sample S2 analytes were in agreement with the robust averages of participants' results, within their respective associated uncertainties.

Table 28 Reference Values for Sample S2 Plum

| Analyte | Reference Value (mg/kg) | Expanded Uncertainty (95%) (mg/kg) | Coverage Factor, k (95%) |
|---|---|---|---|
| Acephate | 0.050 | 0.002 | 2.0 |
| Deltamethrin | 0.048 | 0.003 | 2.0 |
| Endosulfan sulfate | 0.402 | 0.018 | 2.1 |
| Imidacloprid | 0.256 | 0.013 | 2.0 |

Gravimetric measurements for the preparation of calibration solutions and sample blends were traceable to the SI unit for mass (kg) through the Australian national standards for mass. The mass fractions of acephate, deltamethrin, endosulfan sulfate and imidacloprid were traceable to the SI unit of mass (kg) via pure standard reference materials as detailed in Table 29.

Table 29 Details of Pure Reference Materials Used

| Standard | Supplier | Report ID | Batch Number | Purity (95% confidence) |
|---|---|---|---|---|
| Acephate | NIM | GBW(E)060876 | 23001 | 99.8 ± 0.3% |
| Deltamethrin | NIM | GBW(E)060138 | 2303 | 99.8 ± 0.4% |
| Endosulfan sulfate | NMI | P1372.2021.01 | 96-19416 | 97.9 ± 3.0% |
| Imidacloprid | NIM | GBW(E)060996 | 21002 | 99.9 ± 0.2% |

### A2.2 Homogeneity

The samples were prepared using a process previously demonstrated to produce sufficiently homogeneous samples for similar analytes and matrices.

Furthermore, homogeneity testing was conducted for Samples S2 and S3 in this study.

**Sample S2 Homogeneity Testing**

Homogeneity testing was conducted for Sample S2 acephate, deltamethrin, endosulfan sulfate and imidacloprid. The testing was performed by NMI Chemical Reference Values, and was conducted as described above in Section A2.1 Reference Values. Samples were analysed in duplicate and under repeatability conditions.

Homogeneity checks were based on that described by Thompson and Fearn,[16] which is also the procedure described in the International Harmonized Protocol,[4] and these are presented in Tables 30 to 33. Samples were found to be sufficiently homogeneous for use in a PT study with a target SD (as PCV) of 15%.

Table 30 Homogeneity Testing for Sample S2 Acephate

| Bottle Number | S2 Acephate (mg/kg) | |
|---|---|---|
| | Replicate 1 | Replicate 2 |
| 1 | 0.050 | 0.051 |
| 17 | 0.051 | 0.050 |
| 18 | 0.051 | 0.051 |
| 31 | 0.050 | 0.051 |
| 34 | 0.050 | 0.050 |
| 41 | 0.050 | 0.051 |
| 44 | 0.051 | 0.050 |
| 45 | 0.049 | 0.050 |
| Average | 0.050 | |
| CV | 1.0% | |

Thompson and Fearn Homogeneity Tests[16]

| Test | Value | Critical | Result |
|---|---|---|---|
| Cochran | 0.429 | 0.680 | **Pass** |
| $s_{an}/\sigma$ | 0.066 | 0.500 | **Pass** |
| $s^2_{sam}$ | 0.000 | 0.000 | **Pass** |

Table 31 Homogeneity Testing for Sample S2 Deltamethrin

| Bottle Number | S2 Deltamethrin (mg/kg) | |
|---|---|---|
| | Replicate 1 | Replicate 2 |
| 1 | 0.050 | 0.050 |
| 17 | 0.049 | 0.049 |
| 18 | 0.049 | 0.050 |
| 31 | 0.049 | 0.049 |
| 34 | 0.049 | 0.048 |
| 41 | 0.051 | 0.050 |
| 44 | 0.049 | 0.049 |
| 45 | 0.047 | 0.048 |
| Average | 0.049 | |
| CV | 2.0% | |

Thompson and Fearn Homogeneity Tests[16]

| Test | Value | Critical | Result |
|---|---|---|---|
| Cochran | 0.391 | 0.680 | **Pass** |
| $s_{an}/\sigma$ | 0.101 | 0.500 | **Pass** |
| $s^2_{sam}$ | 0.000 | 0.000 | **Pass** |

Table 32 Homogeneity Testing for Sample S2 Endosulfan Sulfate

| Bottle Number | S2 Endosulfan Sulfate (mg/kg) | |
|---|---|---|
| | Replicate 1 | Replicate 2 |
| 1 | 0.401 | 0.397 |
| 17 | 0.397 | 0.408 |
| 18 | 0.398 | 0.402 |
| 31 | 0.397 | 0.401 |
| 34 | 0.403 | 0.402 |
| 41 | 0.406 | 0.401 |
| 44 | 0.401 | 0.401 |
| 45 | 0.395 | 0.397 |
| Average | 0.400 | |
| CV | 0.84% | |

Thompson and Fearn Homogeneity Tests[16]

| Test | Value | Critical | Result |
|---|---|---|---|
| Cochran | 0.592 | 0.680 | **Pass** |
| $s_{an}/\sigma$ | 0.058 | 0.500 | **Pass** |
| $s^2_{sam}$ | 0.000 | 0.001 | **Pass** |

Table 33 Homogeneity Testing for Sample S2 Imidacloprid

| Bottle Number | S2 Imidacloprid (mg/kg) | |
|---|---|---|
| | Replicate 1 | Replicate 2 |
| 1 | 0.255 | 0.254 |
| 17 | 0.254 | 0.255 |
| 18 | 0.255 | 0.254 |
| 31 | 0.255 | 0.252 |
| 34 | 0.251 | 0.255 |
| 41 | 0.254 | 0.253 |
| 44 | 0.251 | 0.255 |
| 45 | 0.254 | 0.254 |
| Average | 0.254 | |
| CV | 0.50% | |

Thompson and Fearn Homogeneity Tests[16]

| Test | Value | Critical | Result |
|---|---|---|---|
| Cochran | 0.449 | 0.680 | **Pass** |
| $s_{an}/\sigma$ | 0.041 | 0.500 | **Pass** |
| $s^2_{sam}$ | 0.000 | 0.000 | **Pass** |

**Sample S3 Homogeneity Testing**

Homogeneity testing was conducted for Sample S3 cyprodinil and endosulfan sulfate. The testing was performed by NMI Food and Health Chemistry Laboratory. Samples were analysed in duplicate under repeatability conditions.

Extraction was performed using the C6 extraction method. The samples were prepared by accurately weighing 10 g of the sample and adding water (1 mL). Methanol (20 mL) was then added, and the solution was shaken and centrifuged. Cyprodinil was analysed using LC. An aliquot of the methanol solution (5 mL) was taken and mixed with a 20 g/100 mL NaCl in $H_2O$ solution (2 mL). An aliquot of the salted solution (5 mL) was then transferred to a Chem-Elute column and eluted with dichloromethane (20 mL). The eluate was evaporated to dryness and the residue dissolved in methanol/MilliQ water (50:50) and filtered through a 0.2 µm filter into a LC vial for LC-MS/MS analysis. Extracts were analysed using a Waters H-Class Acquity UPLC with a XEVO TQD MS/MS Detector. Separation was performed on a Waters Acquity UPLC BEH C18 1.7 µm analytical LC column. Endosulfan sulfate was analysed using GC. An aliquot (5 mL) was taken out of the methanol extract described above, then acetone (5 mL) was added. The solution was shaken to mix well. An aliquot (5 mL) was then transferred to a Chem-Elute column and eluted with 20 mL of dichloromethane. The evaporated residue was dissolved in acetonitrile and filtered through a 0.2 µm filter into a GC vial for GC-MS/MS analysis. Extracts were analysed using an Agilent 7890 GC with an Agilent 7000C QQQ Detector. Separation was performed on an Agilent HP5MS 15 m x 0.25 mm ID x 0.25 µm film thickness analytical GC column.

Homogeneity checks were performed as described above,[4,16] and these are presented in Tables 34 and 35. Samples were found to be sufficiently homogeneous for use in a PT study with a target SD (as PCV) of 20%.

Table 34 Homogeneity Testing for Sample S3 Cyprodinil

| Bottle Number | S3 Cyprodinil (mg/kg) | |
|---|---|---|
| | Replicate 1 | Replicate 2 |
| 2 | 1.39 | 1.37 |
| 6 | 1.40 | 1.38 |
| 11 | 1.36 | 1.39 |
| 13 | 1.45 | 1.53 |
| 20 | 1.36 | 1.40 |
| 27 | 1.25 | 1.26 |
| 35 | 1.35 | 1.48 |
| Average | 1.38 | |
| CV | 5.3% | |

Thompson and Fearn Homogeneity Tests[16]

| Test | Value | Critical | Result |
|---|---|---|---|
| Cochran | 0.646 | 0.727 | **Pass** |
| $s_{an}/\sigma$ | 0.156 | 0.500 | **Pass** |
| $s^2_{sam}$ | 0.004 | 0.017 | **Pass** |

Table 35 Homogeneity Testing for Sample S3 Endosulfan Sulfate

| Bottle Number | S3 Endosulfan Sulfate (mg/kg) | |
|---|---|---|
| | Replicate 1 | Replicate 2 |
| 2 | 0.40 | 0.37 |
| 6 | 0.41 | 0.40 |
| 11 | 0.39 | 0.44 |
| 13 | 0.40 | 0.44 |
| 20 | 0.40 | 0.37 |
| 27 | 0.40 | 0.33 |
| 35 | 0.37 | 0.38 |
| Average | 0.39 | |
| CV | 7.0% | |

Thompson and Fearn Homogeneity Tests[16]

| Test | Value | Critical | Result |
|---|---|---|---|
| Cochran | 0.505 | 0.727 | **Pass** |
| $s_{an}/\sigma$ | 0.342 | 0.500 | **Pass** |
| $s^2_{sam}$ | 0.000 | 0.002 | **Pass** |

## Comparison of Participants' Results and Bottle Numbers

Participants' results in this study also gave no reason to question the samples' homogeneity. Comparisons of results for all scored analytes to bottle number analysed by participants are presented in Figures 50 to 62. Results have only been included if the bottle number was known (i.e. when the participant was sent only one sample set), and results excluded from statistical calculations in Section 5 have been removed. No fill order trend was observed.

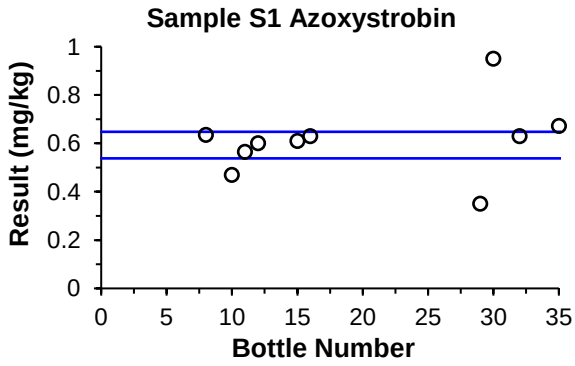



Figure 50 S1 Azoxystrobin Result vs Bottle Number

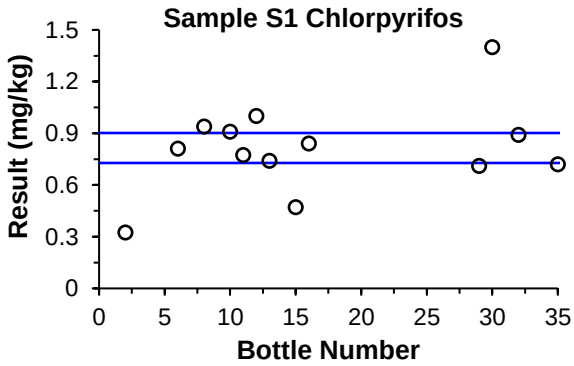



Figure 51 S1 Chlorpyrifos Result vs Bottle Number

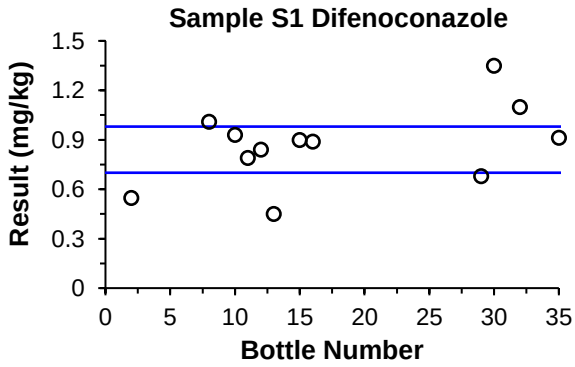



Figure 52 S1 Difenoconazole Result vs Bottle Number

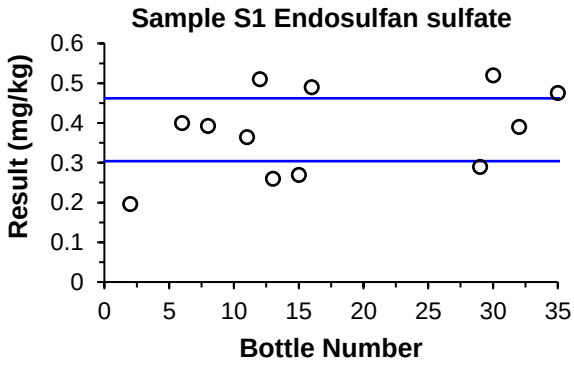



Figure 53 S1 Endosulfan Sulfate Result vs Bottle Number

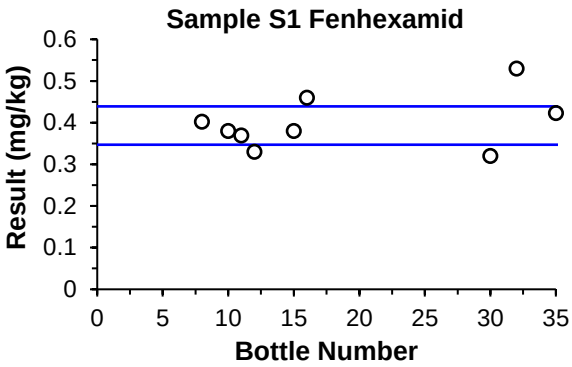



Figure 54 S1 Fenhexamid Result vs Bottle Number

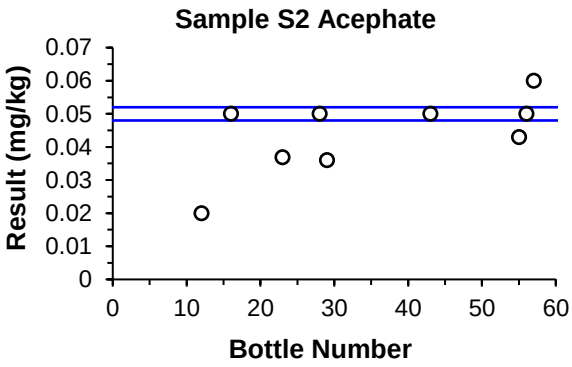



Figure 55 S2 Acephate Result vs Bottle Number

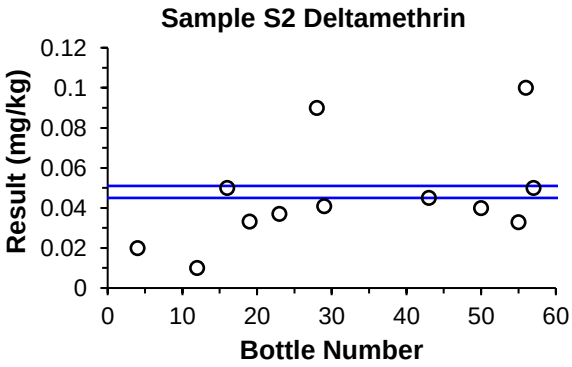



Figure 56 S2 Deltamethrin Result vs Bottle Number

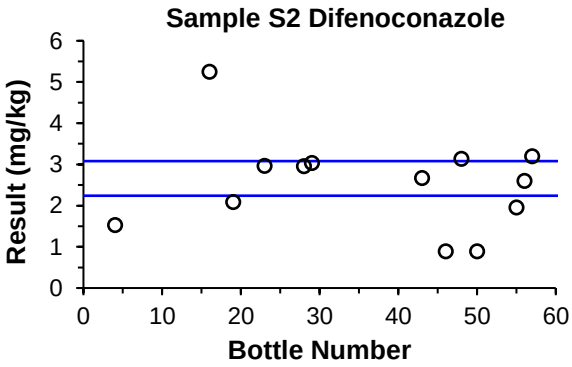



Figure 57 S2 Difenoconazole Result vs Bottle Number

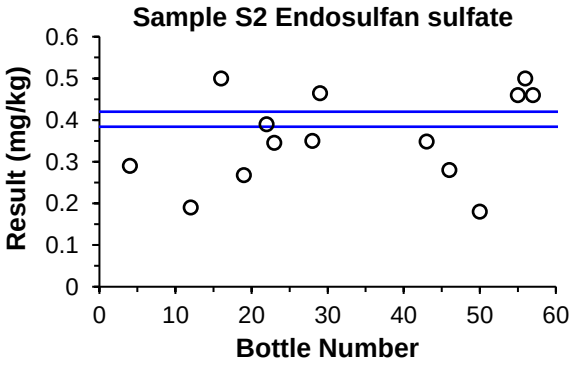



Figure 58 S2 Endosulfan Sulfate Result vs Bottle Number

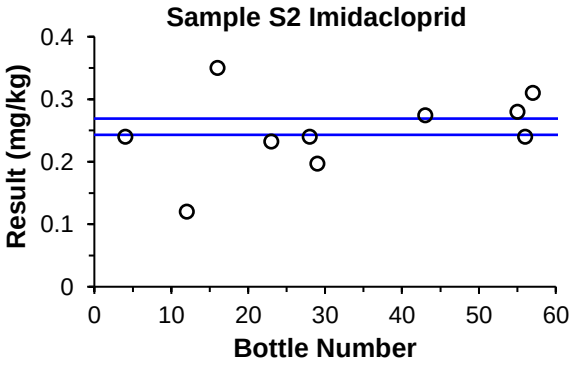



Figure 59 S2 Imidacloprid Result vs Bottle Number

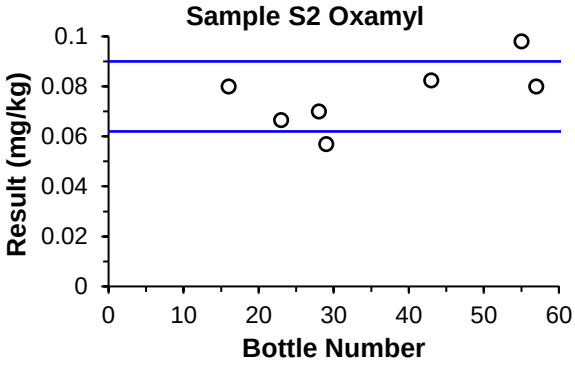



Figure 60 S2 Oxamyl Result vs Bottle Number

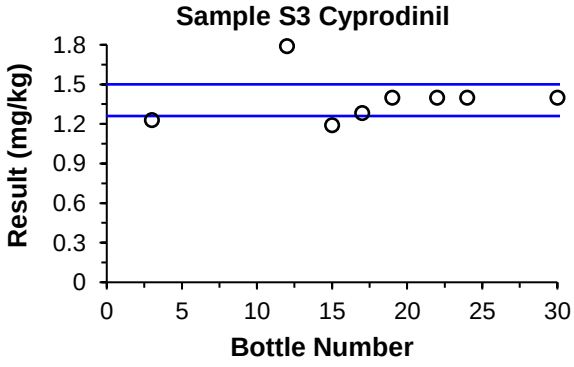



Figure 61 S3 Cyprodinil Result vs Bottle Number

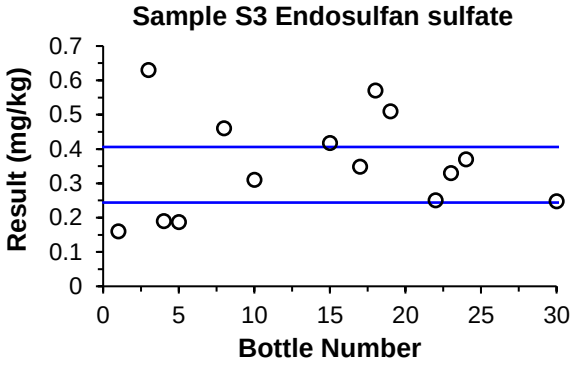



Figure 62 S3 Endosulfan Sulfate Result vs Bottle Number

### A2.3 Stability

The samples were prepared, stored and dispatched using a process previously demonstrated to produce sufficiently stable samples for similar analytes and matrices over a similar time frame. After preparation and before dispatch, samples were stored in a freezer at approximately -20 °C. For dispatch, samples were packaged into insulated polystyrene foam boxes with cooler bricks.

Furthermore, stability testing was conducted for Samples S2 and S3 in this study. Samples were taken from the freezer and packaged in the same way as the samples dispatched to participants. The samples were then stored at ambient conditions for the same amount of time as for the longest participant sample delivery time; for this study, this was 9 days. The samples were then returned to the freezer, and samples were analysed after the study results due date. Therefore, these stability samples reflect both transportation stability as well as stability over the course of the PT study at standard storage conditions.

**Sample S2 Stability Testing**

Stability testing was conducted for Sample S2 acephate, deltamethrin, endosulfan sulfate and imidacloprid. The testing was performed by NMI Chemical Reference Values, and was conducted as described above in Section A2.1 Reference Values.

Figures 63 to 66 present the spiked value (SV), homogeneity value (HV), stability testing results, and the final assigned value (AV) for each analyte. Results were in agreement with each other and the assigned value within their respective uncertainties. The samples were shown to be adequately stable when assessed against the criteria specified in ISO 13528.[7]

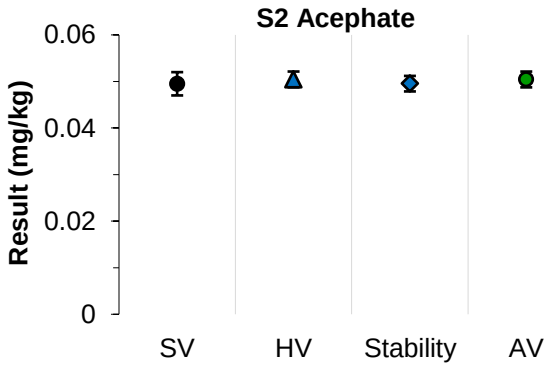



Figure 63 S2 Acephate Stability Results

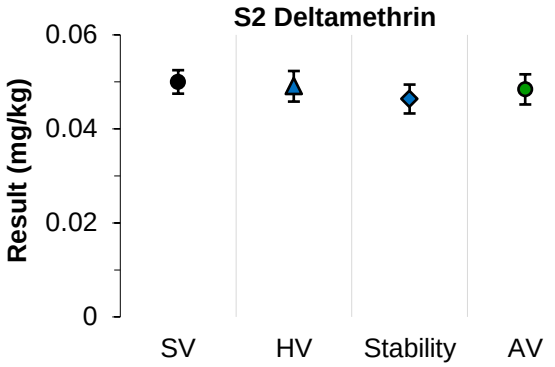



Figure 64 S2 Deltamethrin Stability Results

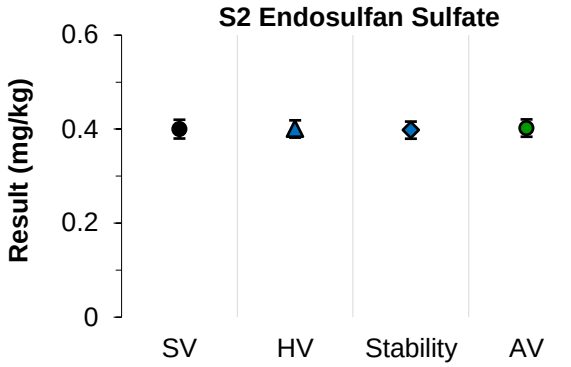



Figure 65 S2 Endosulfan Sulfate Stability Results

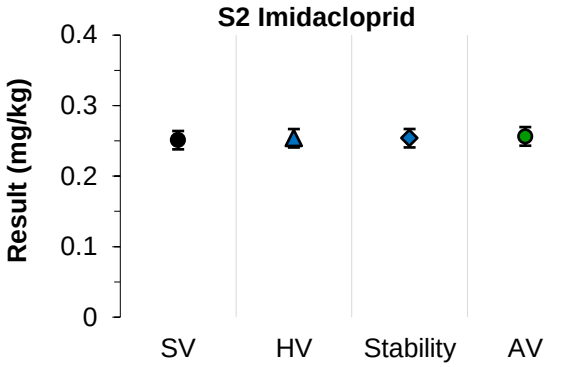



Figure 66 S2 Imidacloprid Stability Results

**Sample S3 Stability Testing**

Stability testing was conducted for Sample S3 cyprodinil and endosulfan sulfate. The testing was performed by NMI Food and Health Chemistry Laboratory and was conducted as described above in Section A2.2 Homogeneity (Sample S3 Homogeneity Testing).

Figures 67 and 68 present the SV, HV, stability testing results, and the final AV for these analytes. Results were in agreement with each other within their respective uncertainties. The samples were shown to be sufficiently stable when assessed against the criteria specified in ISO 13528.[7]

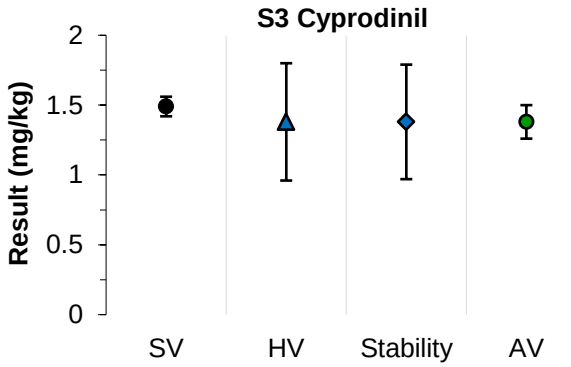



Figure 67 S3 Cyprodinil Stability Results

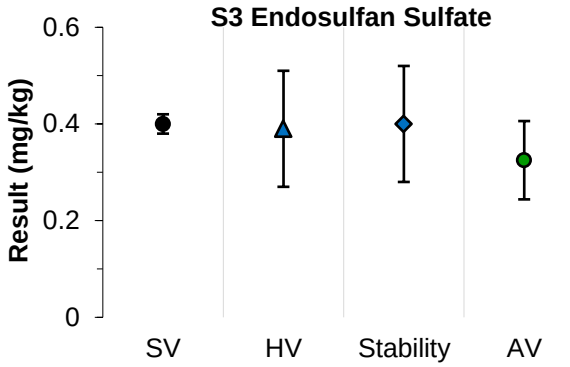
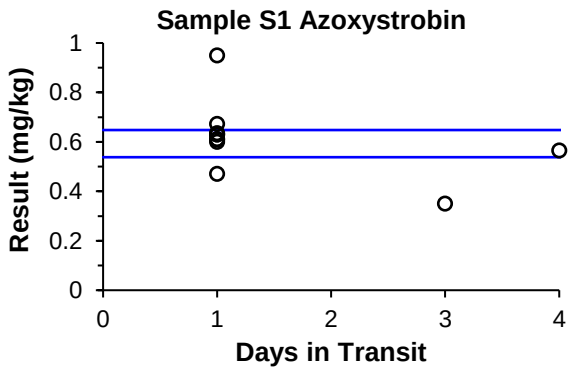



Figure 68 S3 Endosulfan Sulfate Stability Results

**Comparison of Participants' Results and Sample Transit Time**

Participants' results in this study also gave no reason to question the samples' transportation stability. Comparisons of results for all scored analytes to days spent in transit are presented in Figures 69 to 81. Results excluded from statistical calculations in Section 5 have been removed.



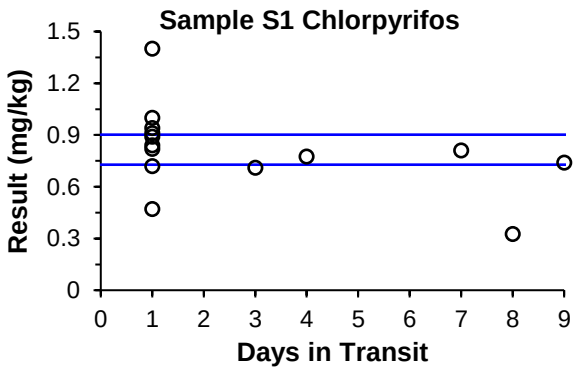



Figure 69 S1 Azoxystrobin Result vs Transit Days

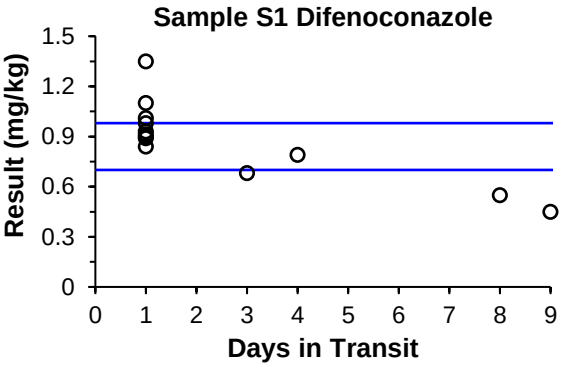



Figure 70 S1 Chlorpyrifos Result vs Transit Days

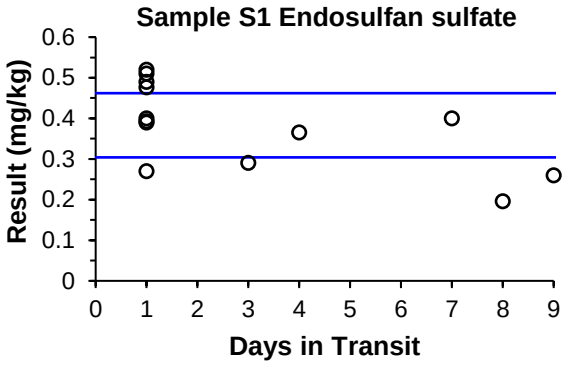
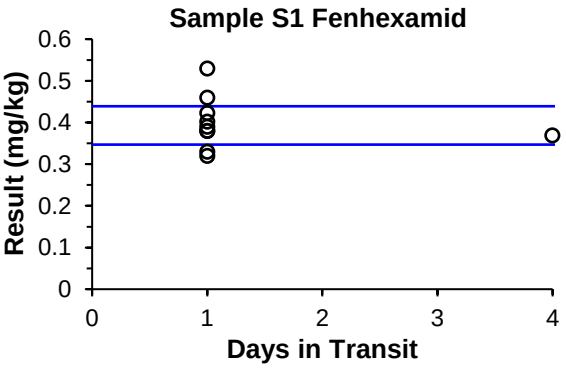



Figure 71 S1 Difenoconazole Result vs Transit Days

Figure 72 S1 Endosulfan Sulfate Result vs Transit Days



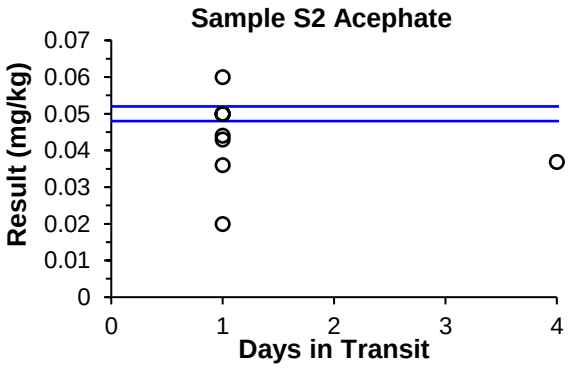
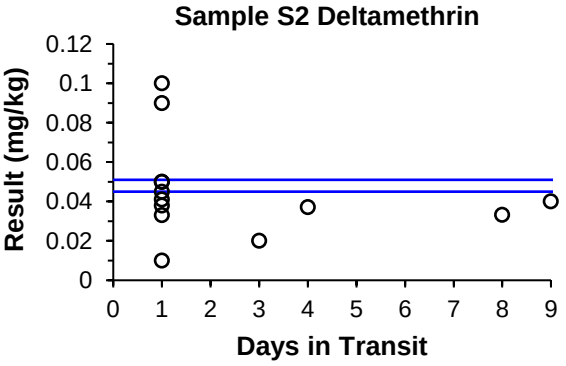




Figure 73 S1 Fenhexamid Result vs Transit Days

Figure 74 S2 Acephate Result vs Transit Days



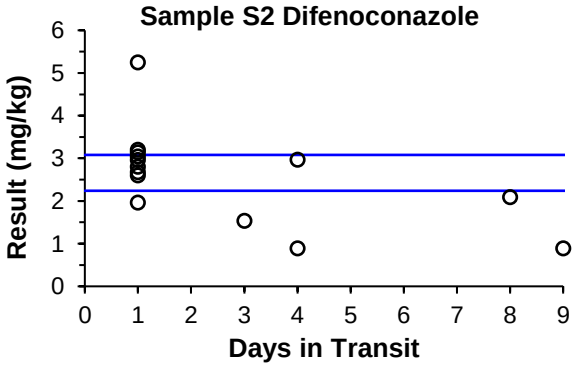
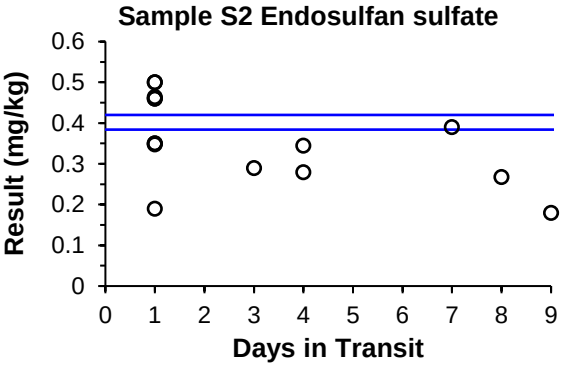




Figure 75 S2 Deltamethrin Result vs Transit Days

Figure 76 S2 Difenoconazole Result vs Transit Days



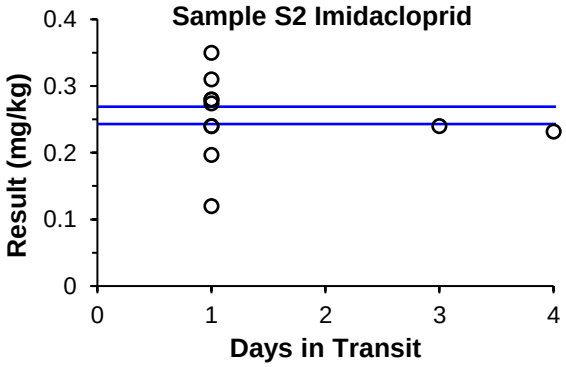



Figure 77 S2 Endosulfan Sulfate Result vs Transit Days

Figure 78 S2 Imidacloprid Result vs Transit Days

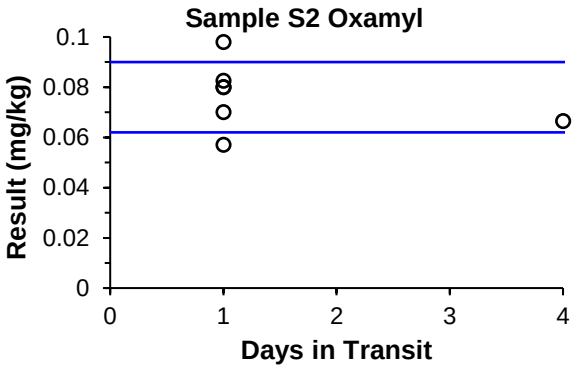



Figure 79 S2 Oxamyl Result vs Transit Days

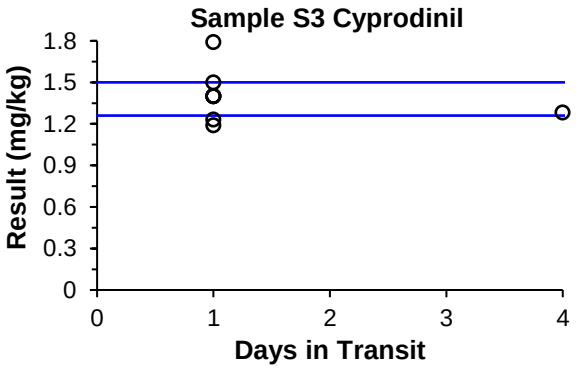



Figure 80 S3 Cyprodinil Result vs Transit Days

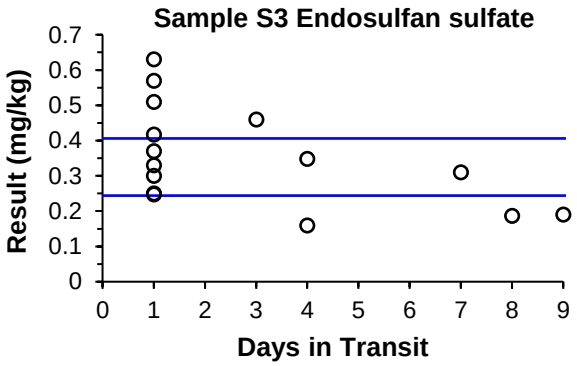



Figure 81 S3 Endosulfan Sulfate Result vs Transit Days

## APPENDIX 3 ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY, z-SCORE AND $E_n$-SCORE CALCULATIONS

### A3.1 Robust Average and Associated Uncertainty

Robust averages were calculated using the procedure described in ISO 13528.[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 Sample S1 fenhexamid is set out below in Table 36.

Table 36 Uncertainty of Robust Average for Sample S1 Fenhexamid

| | |
|---|---|
| Number of results ($p$) | 10 |
| Robust Average | 0.393 mg/kg |
| $S_{rob\ av}$ | 0.058 mg/kg |
| $u_{rob\ av}$ | 0.023 mg/kg |
| $k$ | 2 |
| $U_{rob\ av}$ | 0.046 mg/kg |

Therefore, the robust average for Sample S1 fenhexamid is 0.393 ± 0.046 mg/kg.

### A3.2 z-Score and $E_n$-Score Calculation

For each participant's result, a *z*-score and $E_n$-score are calculated according to Equations 2 and 3 respectively (Section 4).

A worked example for the result reported by Laboratory 1 for Sample S1 azoxystrobin is set out below in Table 37.

Table 37 *z*-Score and $E_n$-Score for Sample S1 Azoxystrobin Result Reported by Laboratory 1

| Participant Result (mg/kg) | Assigned Value (mg/kg) | Target Standard Deviation | *z*-Score | $E_n$-Score |
|---|---|---|---|---|
| 0.60 ± 0.14 | 0.593 ± 0.055 | 15% as CV, or: 0.15 × 0.593 = 0.08895 mg/kg | $z = \frac{0.60 - 0.593}{0.08895} = 0.08$ | $E_n = \frac{0.60 - 0.593}{\sqrt{0.14^2 + 0.055^2}} = 0.05$ |

## APPENDIX 4 PARTICIPANTS' TEST METHODS

Participants were requested to provide information about their test methods. Responses are presented in Tables 38 to 52. Some responses may be modified so that the participant cannot be identified.

Table 38 Sample S1 Tomato Azoxystrobin Methodology

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | 10 | QuEChERS | Acetonitrile | PSA / C18 | LC-MS/MS |
| 2 | NT | | | | |
| 3 | 10 | QuEChERS | Acetonitrile | PTFE | LC-MS/MS |
| 4 | 20 | Solid-Liquid | DCM | | LC/GC-MS/MS |
| 5 | 15 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 6 | NT | | | | |
| 7 | 10 | QuEChERS | Acetonitrile | Dispersive SPE | LC-MS/MS |
| 8 | NT | | | | |
| 9 | 10 | Solid-Liquid | ACN | carbon/C18/Florisil | GC-MS |
| 10 | 5 | QuEChERS | Acetonitrile | Dispersive SPE:- PSA, C18, MgSO4. | GC-MS/MS |
| 11 | 10 | QuEChERS | Acetonitrile | N/A | LC-MS/MS |
| 12 | 10 | QuEChERS | ACN | d-SPE | LC-MS/MS |
| 13 | 10 | QuEChERS | Acetonitrile | PSA/Carbon | GC MS |
| 14 | NR | | | | |
| 15 | NT | | | | |
| 16 | 5 | QUECHER | Acetonitrile | PSA | LC-MS/MS |

Table 39 Sample S1 Tomato Chlorpyrifos Methodology

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | 10 | QuEChERS | Acetonitrile | PSA / C18 | GC-MS/MS |

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 2 | 10 | QuEChERS | acetonitrile | dSPE | GC-MS |
| 3 | 10 | QuEChERS | Acetonitrile | Florisil | GC-MS/MS |
| 4 | 20 | Solid-Liquid | DCM | | LC/GC-MS/MS |
| 5 | 15 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 6 | 10 | QuEChERS | acidified Acetonitrile | dSPE with PSA | GC-MS/MS |
| 7 | 10 | QuEChERS | Acetonitrile | Dispersive SPE | GC-MS/MS |
| 8 | 10 | Solid-Liquid | Acetonitrile | dSPE | GC-MS |
| 9 | 10 | Solid-Liquid | ACN | carbon/C18/Florisil | GC-MS |
| 10 | 5 | QuEChERS | Acetonitrile | Dispersive SPE:- PSA, C18, MgSO4. | GC-MS/MS |
| 11 | 10 | QuEChERS | Acetonitrile | PSA | GC-MS/MS |
| 12 | 10 | QuEChERS | ACN | d-SPE | GC-MS/MS |
| 13 | 10 | QuEChERS | Acetonitrile | PSA/Carbon | GC MS |
| 14 | NR | | | | |
| 15 | 10 | QuEChERS | Acetonitrile | 150mg PSA, 900mg MgSO4 | GC-FPD, GC-MS |
| 16 | 5 | QUECHER | Acetonitrile | PSA | GC-MS/MS |

Table 40 Sample S1 Tomato Difenoconazole Methodology

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | 10 | QuEChERS | Acetonitrile | PSA / C18 | LC-MS/MS |
| 2 | 10 | SPE | acetonitrile | C18,Envicarb, Florisil | GC-ECD |
| 3 | 10 | QuEChERS | Acetonitrile | PTFE | LC-MS/MS |
| 4 | 20 | Solid-Liquid | DCM | | LC/GC-MS/MS |
| 5 | 15 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 6 | NT | | | | |

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 7 | 10 | QuEChERS | Acetonitrile | Dispersive SPE | LC-MS/MS |
| 8 | 10 | Solid-Liquid | Acetonitrile | dSPE | GC-MS |
| 9 | 10 | Solid-Liquid | ACN | carbon/C18/Florisil | GC-MS |
| 10 | 5 | QuEChERS | Acetonitrile | Dispersive SPE:- C18, MgSO4. | LC-MS/MS |
| 11 | 10 | QuEChERS | Acetonitrile | N/A | LC-MS/MS |
| 12 | 10 | QuEChERS | ACN | d-SPE | LC-MS/MS |
| 13 | 10 | QuEChERS | Acetonitrile | PSA/Carbon | GC MS |
| 14 | NR | | | | |
| 15 | NT | | | | |
| 16 | 5 | QUECHER | Acetonitrile | PSA | GC-MS/MS |

Table 41 Sample S1 Tomato Endosulfan Sulfate Methodology

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | 10 | QuEChERS | Acetonitrile | PSA / C18 | GC-MS/MS |
| 2 | 10 | SPE | acetonitrile | C18,Envicarb, Florisil | GC-ECD |
| 3 | 10 | QuEChERS | Acetonitrile | Florisil | GC-MS/MS |
| 4 | 20 | Solid-Liquid | DCM | | GC-MS/MS |
| 5 | NT | | | | |
| 6 | NT | | | | |
| 7 | 10 | QuEChERS | Acetonitrile | Dispersive SPE | GC-MS/MS |
| 8 | 10 | Solid-Liquid | Acetonitrile | dSPE | GC-MS |
| 9 | 10 | Solid-Liquid | ACN | carbon/C18/Florisil | GC-MS |
| 10 | 5 | QuEChERS | Acetonitrile | Dispersive SPE:- PSA, C18, MgSO4. | GC-MS/MS |
| 11 | 10 | QuEChERS | Acetonitrile | PSA | GC-MS/MS |

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 12 | 10 | QuEChERS | ACN | d-SPE | GC-MS/MS |
| 13 | 10 | QuEChERS | Acetonitrile | PSA/Carbon | GC MS |
| 14 | NR | | | | |
| 15 | 10 | QuEChERS | Acetonitrile | 150mg PSA, 900mg MgSO4 | GC-ECD, GC-MS |
| 16 | 5 | QUECHER | Acetonitrile | PSA | GC-MS/MS |

Table 42 Sample S1 Tomato Fenhexamid Methodology

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | 10 | QuEChERS | Acetonitrile | PSA / C18 | LC-MS/MS |
| 2 | NT | | | | |
| 3 | 10 | QuEChERS | Acetonitrile | PTFE | LC-MS/MS |
| 4 | 20 | Solid-Liquid | DCM | | LC/GC-MS/MS |
| 5 | 15 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 6 | NT | | | | |
| 7 | 10 | QuEChERS | Acetonitrile | Dispersive SPE | LC-MS/MS |
| 8 | NT | | | | |
| 9 | NT | | | | |
| 10 | 5 | QuEChERS | Acetonitrile | Dispersive SPE:- C18, MgSO4. | LC-MS/MS |
| 11 | 10 | QuEChERS | Acetonitrile | N/A | LC-MS/MS |
| 12 | 10 | QuEChERS | ACN | d-SPE | GC-MS/MS |
| 13 | NT | | | | |
| 14 | NR | | | | |
| 15 | NT | | | | |
| 16 | 5 | QUECHER | Acetonitrile | PSA | LC-MS/MS |

Table 43 Sample S2 Plum Acephate Methodology

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | 10 | QuEChERS | Acetonitrile | PSA / C18 | LC-MS/MS |
| 2 | NT | | | | |
| 3 | 10 | QuEChERS | Acetonitrile | PTFE | LC-MS/MS |
| 4 | 20 | Solid-Liquid | DCM | | LC-MS/MS |
| 5 | NT | | | | |
| 6 | NR | | | | |
| 7 | 10 | QuEChERS | Acetonitrile | Dispersive SPE | LC-MS/MS |
| 8 | NT | | | | |
| 9 | NT | | | | |
| 10 | 5 | QuEChERS | Acetonitrile | Dispersive SPE:- C18, MgSO4. | LC-MS/MS |
| 11 | 10 | QuEChERS | Acetonitrile | N/A | LC-MS/MS |
| 12 | 10 | QuEChERS | ACN | d-SPE | LC-MS/MS |
| 13 | NT | | | | |
| 14 | NR | | | | |
| 15 | NT | | | | |
| 16 | 5 | QUECHER | Acetonitrile | PSA | LC-MS/MS |

Table 44 Sample S2 Plum Deltamethrin Methodology

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | 10 | QuEChERS | Acetonitrile | PSA / C18 | GC-MS/MS |
| 2 | 10 | QuEChERS | acetonitrile | dSPE | GC-MS |
| 3 | 10 | QuEChERS | Acetonitrile | Florisil | GC-MS/MS |
| 4 | 20 | Solid-Liquid | DCM | | GC-MS/MS |

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 5 | NT | | | | |
| 6 | NR | | | | |
| 7 | 10 | QuEChERS | Acetonitrile | Dispersive SPE | GC-MS/MS |
| 8 | 10 | Solid-Liquid | Acetonitrile | dSPE | GC-MS |
| 9 | 10 | Solid-Liquid | ACN | carbon/C18/Florisil | GC-MS |
| 10 | 5 | QuEChERS | Acetonitrile | Dispersive SPE:- PSA, C18, MgSO4. | GC-MS/MS |
| 11 | 10 | QuEChERS | Acetonitrile | N/A | LC-MS/MS |
| 12 | 10 | QuEChERS | ACN | d-SPE | GC-MS/MS |
| 13 | 10 | QuEChERS | Acetonitrile | PSA/Carbon | GC MS |
| 14 | NR | | | | |
| 15 | NR | | | | |
| 16 | 5 | QUECHER | Acetonitrile | PSA | GC-MS/MS |

Table 45 S2 Plum Difenoconazole Methodology

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | 10 | QuEChERS | Acetonitrile | PSA / C18 | LC-MS/MS |
| 2 | 10 | SPE | acetonitrile | C18,Envicarb, Florisil | GC-ECD |
| 3 | 10 | QuEChERS | Acetonitrile | PTFE | LC-MS/MS |
| 4 | 20 | Solid-Liquid | DCM | | LC/GC-MS/MS |
| 5 | 15 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 6 | NT | | | | |
| 7 | 10 | QuEChERS | Acetonitrile | Dispersive SPE | LC-MS/MS |
| 8 | 10 | Solid-Liquid | Acetonitrile | dSPE | GC-MS |
| 9 | 10 | Solid-Liquid | ACN | carbon/C18/Florisil | GC-MS |

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 10 | 5 | QuEChERS | Acetonitrile | Dispersive SPE:- C18, MgSO4. | LC-MS/MS |
| 11 | 10 | QuEChERS | Acetonitrile | N/A | LC-MS/MS |
| 12 | 10 | QuEChERS | ACN | d-SPE | LC-MS/MS |
| 13 | 10 | QuEChERS | Acetonitrile | PSA/Carbon | GC MS |
| 14 | NR | | | | |
| 15 | NT | | | | |
| 16 | 5 | QUECHER | Acetonitrile | PSA | GC-MS/MS |

Table 46 Sample S2 Plum Endosulfan Sulfate Methodology

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | 10 | QuEChERS | Acetonitrile | PSA / C18 | GC-MS/MS |
| 2 | 10 | SPE | acetonitrile | C18,Envicarb, Florisil | GC-ECD |
| 3 | 10 | QuEChERS | Acetonitrile | Florisil | GC-MS/MS |
| 4 | 20 | Solid-Liquid | DCM | | GC-MS/MS |
| 5 | NT | | | | |
| 6 | NR | | | | |
| 7 | 10 | QuEChERS | Acetonitrile | Dispersive SPE | GC-MS/MS |
| 8 | 10 | Solid-Liquid | Acetonitrile | dSPE | GC-MS |
| 9 | 10 | Solid-Liquid | ACN | carbon/C18/Florisil | GC-MS |
| 10 | 5 | QuEChERS | Acetonitrile | Dispersive SPE:- PSA, C18, MgSO4. | GC-MS/MS |
| 11 | 10 | QuEChERS | Acetonitrile | PSA | GC-MS/MS |
| 12 | 10 | QuEChERS | ACN | d-SPE | GC-MS/MS |
| 13 | 10 | QuEChERS | Acetonitrile | PSA/Carbon | GC MS |
| 14 | NR | | | | |

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 15 | 10 | QuEChERS | Acetonitrile | 150mg PSA, 45mg GCB, 855mg MgSO4 | GC-ECD, GC-MS |
| 16 | 5 | QUECHER | Acetonitrile | PSA | GC-MS/MS |

Table 47 Sample S2 Plum Imidacloprid Methodology

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | 10 | QuEChERS | Acetonitrile | PSA / C18 | LC-MS/MS |
| 2 | NT | | | | |
| 3 | 10 | QuEChERS | Acetonitrile | PTFE | LC-MS/MS |
| 4 | 20 | Solid-Liquid | DCM | | LC-MS/MS |
| 5 | NT | | | | |
| 6 | NR | | | | |
| 7 | 10 | QuEChERS | Acetonitrile | Dispersive SPE | LC-MS/MS |
| 8 | NT | | | | |
| 9 | 10 | Solid-Liquid | ACN | carbon/C18/Florisil | GC-MS |
| 10 | 5 | QuEChERS | Acetonitrile | Dispersive SPE:- C18, MgSO4. | LC-MS/MS |
| 11 | 10 | QuEChERS | Acetonitrile | N/A | LC-MS/MS |
| 12 | 10 | QuEChERS | ACN | d-SPE | LC-MS/MS |
| 13 | NT | | | | |
| 14 | NR | | | | |
| 15 | NT | | | | |
| 16 | 5 | QUECHER | Acetonitrile | PSA | LC-MS/MS |

Table 48 Sample S2 Plum Oxamyl Methodology

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | NT | | | | |

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 2 | NT | | | | |
| 3 | 10 | QuEChERS | Acetonitrile | PTFE | LC-MS/MS |
| 4 | 20 | Solid-Liquid | DCM | | LC-MS/MS |
| 5 | NT | | | | |
| 6 | NT | | | | |
| 7 | 10 | QuEChERS | Acetonitrile | Dispersive SPE | LC-MS/MS |
| 8 | NT | | | | |
| 9 | NT | | | | |
| 10 | 5 | QuEChERS | Acetonitrile | Dispersive SPE:- PSA, C18, MgSO4. | GC-MS/MS |
| 11 | 10 | QuEChERS | Acetonitrile | N/A | LC-MS/MS |
| 12 | 10 | QuEChERS | ACN | d-SPE | GC-MS/MS |
| 13 | NT | | | | |
| 14 | NR | | | | |
| 15 | NT | | | | |
| 16 | 5 | QUECHER | Acetonitrile | PSA | LC-MS/MS |

Table 49 Sample S3 Garlic Cyprodinil Methodology

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | 5 | QuEChERS | Acetonitrile | PSA / C18 | LC-MS/MS |
| 2 | NT | | | | |
| 3 | 10 | QuEChERS | Acetonitrile | PTFE | LC-MS/MS |
| 4 | 20 | Solid-Liquid | DCM | | LC/GC-MS/MS |
| 5 | 15 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 6 | NR | | | | |

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 7 | 10 | QuEChERS | Acetonitrile | Dispersive SPE | GC-MS/MS |
| 8 | NT | | | | |
| 9 | NT | | | | |
| 10 | 5 | QuEChERS | Acetonitrile | Dispersive SPE:- C18, MgSO4. | LC-MS/MS |
| 11 | 10 | QuEChERS | Acetonitrile | N/A | LC-MS/MS |
| 12 | 10 | QuEChERS | ACN | d-SPE | LC-MS/MS |
| 13 | NT | | | | |
| 14 | NR | | | | |
| 15 | NT | | | | |
| 16 | 5 | QUECHER | Acetonitrile | PSA | GC-MS/MS |

Table 50 Sample S3 Endosulfan Sulfate Methodology

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | 5 | QuEChERS | Acetonitrile | PSA / C18 | GC-MS/MS |
| 2 | 10 | QuEChERS | acetonitrile | dSPE | GC-ECD |
| 3 | 10 | QuEChERS | Acetonitrile | Florisil | GC-MS/MS |
| 4 | 20 | Solid-Liquid | DCM | | GC-MS/MS |
| 5 | NT | | | | |
| 6 | NR | | | | |
| 7 | 10 | QuEChERS | Acetonitrile | Dispersive SPE | GC-MS/MS |
| 8 | 5 | Solid-Liquid | Acetonitrile | dSPE | GC-MS |
| 9 | 5 | Liquid-Liquid | ACN | N/A | GC-MS |
| 10 | 5 | QuEChERS | Acetonitrile | Dispersive SPE:- PSA, C18, MgSO4. | GC-MS/MS |
| 11 | 10 | QuEChERS | Acetonitrile | PSA | GC-MS/MS |

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 12 | 10 | QuEChERS | ACN | d-SPE | GC-MS/MS |
| 13 | 10 | QuEChERS | Acetonitrile | PSA/Carbon | GC MS |
| 14 | NR | | | | |
| 15 | 5 | QuEChERS | Acetonitrile | 400mg PSA, 400mg GCB, 400mg C18EC, 1200mg MgSO4 | GC-ECD, GC-MS |
| 16 | 5 | QUECHER | Acetonitrile | PSA | GC-MS/MS |

Table 51 Sample S3 Garlic Maleic Hydrazide Methodology

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | NT | | | | |
| 2 | NT | | | | |
| 3 | 10 | QuEChERS | Acetonitrile | PTFE | LC-MS/MS |
| 4 | NT | | | | |
| 5 | NT | | | | |
| 6 | NT | | | | |
| 7 | NT | | | | |
| 8 | NT | | | | |
| 9 | NT | | | | |
| 10 | 2.5 | SPE | Water | Accucat | LC-MS/MS |
| 11 | NT | | | | |
| 12 | NT | | | | |
| 13 | NT | | | | |
| 14 | NT | | | | |
| 15 | NT | | | | |
| 16 | 5 | QuPPe | Methanol/water | | LC-MS/MS |

Table 52 Sample S3 Garlic Spirotetramat Methodology

| Lab. Code | Sample Mass for Analysis (g) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | 5 | QuEChERS | Acetonitrile | PSA / C18 | LC-MS/MS |
| 2 | NT | | | | |
| 3 | 10 | QuEChERS | Acetonitrile | PTFE | LC-MS/MS |
| 4 | 20 | Solid-Liquid | DCM | | LC-MS/MS |
| 5 | NR | | | | |
| 6 | NR | | | | |
| 7 | NT | | | | |
| 8 | NT | | | | |
| 9 | NT | | | | |
| 10 | 5 | QuEChERS | Acetonitrile | Dispersive SPE:- C18, MgSO4. | LC-MS/MS |
| 11 | 10 | QuEChERS | Acetonitrile | N/A | LC-MS/MS |
| 12 | 10 | QuEChERS | ACN | d-SPE | LC-MS/MS |
| 13 | NT | | | | |
| 14 | NR | | | | |
| 15 | NT | | | | |
| 16 | 5 | QUECHER | Acetonitrile | PSA | LC-MS/MS |

## APPENDIX 5 ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| 2,4-D | 2,4-Dichlorophenoxyacetic acid |
| ACN | Acetonitrile |
| AV | Assigned Value |
| CAC/GL | Codex Alimentarius Commission Guidelines |
| CITAC | Cooperation on International Traceability in Analytical Chemistry |
| CRM | Certified Reference Material |
| CV | Coefficient of Variation |
| DCM | Dichloromethane |
| dSPE | Dispersive Solid Phase Extraction |
| ECD | Electron Capture Detection |
| FAO | Food and Agriculture Organization of the United Nations |
| FPD | Flame Photometric Detection |
| GC | Gas Chromatography |
| GCB | Graphitized Carbon Black |
| GUM | Guide to the expression of Uncertainty in Measurement |
| HV | Homogeneity Value |
| IDMS | Isotope Dilution Mass Spectrometry |
| IEC | International Electrotechnical Commission |
| ISO | International Organization for Standardization |
| JMPR | Joint FAO/WHO Meeting on Pesticide Residues |
| k | Coverage factor |
| LC | Liquid Chromatography |
| LLE | Liquid-Liquid Extraction |
| LOR | Limit of Reporting |
| Max | Maximum |
| Md | Median |
| Min | Minimum |
| MRL | Maximum Residue Limit |
| MS | Mass Spectrometry |
| MS/MS | Tandem Mass Spectrometry |
| MU | Measurement Uncertainty |
| N | Number of numeric results |
| NATA | National Association of Testing Authorities, Australia |
| NIM | National Institute of Metrology, China |

| | |
|---|---|
| NMI | National Measurement Institute, Australia |
| NPD | Nitrogen Phosphorus Detection |
| NR | Not Reported |
| NT | Not Tested |
| PCV | Performance Coefficient of Variation |
| PFTE | Polytetrafluoroethylene |
| PSA | Primary/Secondary Amine |
| PT | Proficiency Testing |
| QTOF | Quadrupole Time-Of-Flight Mass Spectrometry |
| QuEChERS | Quick, Easy, Cheap, Effective, Rugged and Safe extraction |
| RA | Robust Average |
| Rec | Recovery |
| RM | Reference Material |
| RV | Reference Value |
| SANTE | Directorate-General for Health and Food Safety |
| SD | Standard Deviation |
| SI | International System of Units |
| SLE | Solid-Liquid Extraction |
| SPE | Solid Phase Extraction |
| SS | Spiked Samples |
| SV | Spiked Value (or the formulated concentration) |
| WHO | World Health Organization |

**END OF REPORT**