Australian Government
Department of Industry, Science and Resources

National Measurement Institute

# Proficiency Test Final Report AQA 22-08 Pesticides in Fruit, Vegetables & Herbs

November 2022

## ACKNOWLEDGMENTS

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

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

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## SUMMARY

AQA 22-08 Pesticides in Fruit, Vegetables & Herbs commenced in May 2022. Twenty laboratories registered to participate, and all participants submitted results.

Four sets of test samples were prepared at the NMI laboratory in Sydney. Samples were prepared by adding pesticide standard solutions to pureed tomatoes (Sample S1), lettuce (Sample S2), parsley (Sample S3) and green beans (Sample S4).

Of a possible 340 results, 231 numeric results (68%) were submitted. Of the remaining results, 16 results were a 'less than' value (<*x*) or Not Reported (NR), and 93 results were Not Tested (NT).

The assigned values for Sample S1 bifenthrin, buprofezin, chlorpyrifos, endosulfan sulfate, imazalil and pirimicarb, and Sample S2 endosulfan sulfate and pirimicarb, were reference values obtained by isotope dilution mass spectrometry. The associated uncertainties were estimated in accordance with the ISO GUM.

**Traceability**: The reference values are traceable to the SI unit for mass (kg) through the Australian national standards for mass and the purity of 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, vegetables and herbs.*

Laboratories **1**, **2**, **7**, **8**, **9**, **11**, **14** and **19** reported numeric results for all 15 scored analytes.

Five participants did not report results for analytes that they tested for and were present in the test samples (total of 16 results).

Three participants reported analytes that were not spiked into the samples (total of five results).

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

Of 201 results for which *z* scores were calculated, 162 (81%) returned $|z| \leq 2.0$, indicating a satisfactory performance.

Of 201 results for which $E_n$ scores were calculated, 145 (72%) returned $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratory **11** returned satisfactory *z* and $E_n$ scores for all scored analytes. Laboratory **14** returned satisfactory *z* scores for all scored analytes.

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

The Australia New Zealand Food Standards Code specifies maximum residue limits for various pesticides in different food products.

Of 135 results assessed, 102 (76%) gave the correct compliance status (inclusive of uncertainty), while 23 (17%) gave conditionally correct compliance statuses (i.e. the result gave the correct compliance status but the uncertainty spanned the maximum residue limit).

Laboratories **9** and **14** returned the correct compliance status for all 10 assessed analytes.

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

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 used was extraction using the QuEChERS procedure, with acetonitrile as the extraction solvent and using LC-MS/MS for analysis.

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

Of 231 numeric results, 207 (90%) were reported with an associated expanded measurement uncertainty. The magnitude of the reported uncertainties was within the range 5.3% to 85% 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 are available for purchase from NMI and can be used for quality control and method validation purposes.

# 1 INTRODUCTION

## 1.1 NMI Proficiency Testing Program

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

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

- pesticide residues in soil, water, fruit, vegetables and herbs;
- petroleum hydrocarbons in soil and water;
- inorganic analytes in soil, water, filters, food and pharmaceuticals;
- per- and polyfluoroalkyl substances in soil, 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, vegetables and herbs;
- compare the performances of participants and assess their accuracy in the measurement of pesticides in fruit, vegetables and herbs;
- assess the ability of participants to determine compliance of pesticides in fruit, vegetables and herbs against regulatory standards;
- evaluate participants' methods for the measurement of pesticides in fruit, vegetables and herbs;
- 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 as a provider of PT schemes.[1] This PT study is within the scope of NMI's accreditation.

## 2 STUDY INFORMATION

### 2.1 Selection of Pesticides and Matrices

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

Table 1 List of Possible Analytes

| | | | |
|---|---|---|---|
| Abamectin | Cypermethrin | Fenthion sulfone | Metrafenone |
| Acetamiprid | Cyprodinil | Fenthion sulfoxide | Mevinphos |
| Azinphos-methyl | 2,4-D | Fenvalerate | Monocrotophos |
| Azoxystrobin | p,p'-DDT | Fludioxonil | Omethoate |
| Bifenazate | Deltamethrin | Glyphosate | Parathion |
| Bifenthrin | Diazinon | Imazalil | Parathion Methyl |
| Buprofezin | Dicofol | Imidacloprid | Penconazole |
| Captan | Dieldrin | Indoxacarb | Permethrin |
| Carbaryl | Dimethoate | Iprodione | Pirimicarb |
| Carbendazim | Dithiocarbamates | Linuron | Procymidone |
| Chlorfenvinphos | alpha-Endosulfan | Maldison | Profenofos |
| Chlorothalonil | beta-Endosulfan | Metalaxyl | Propargite |
| Chlorpyrifos | Endosulfan Sulfate | Methamidophos | Pyraclostrobin |
| Clothianidin | Fenamiphos | Methidathion | Spinosad |
| Cyfluthrin | Fenitrothion | Methomyl | Thiabendazole |
| Cyhalothrin | Fenthion | Methomyl oxime | Triadimefon |

The spiked values for the samples, and corresponding Australian maximum residue limits (MRLs),[5] are presented in Table 2. For matrix and analyte 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;
- current Australian agricultural practice; and
- Australian MRLs in the Australia New Zealand Food Standards Code.[5]

Table 2 Spiked Values of Test Samples

| Sample | Analyte | Spiked Value (mg/kg) | Uncertainty[a] (mg/kg) | MRL[b] (mg/kg) |
|---|---|---|---|---|
| S1 (Tomato) | Bifenthrin | 0.299 | 0.015 | 0.5 |
| | Buprofezin | 0.189 | 0.009 | 1 |
| | Chlorpyrifos | 0.819 | 0.041 | T0.5 |
| | Endosulfan sulfate | 0.647 | 0.032 | - |
| | Imazalil | 0.746 | 0.037 | 0.5 |
| | Imidacloprid | 0.362 | 0.018 | 0.5[c] |
| | Pirimicarb | 0.704 | 0.035 | 1[d] |

| Sample | Analyte | Spiked Value (mg/kg) | Uncertainty[a] (mg/kg) | MRL[b] (mg/kg) |
|---|---|---|---|---|
| S2 (Lettuce) | Endosulfan sulfate | 0.732 | 0.037 | - |
| | Metalaxyl | 0.452 | 0.023 | 0.3 |
| | Permethrin | 0.152 | 0.008 | 5[e] |
| | Pirimicarb | 0.697 | 0.035 | 7[d] |
| S3 (Parsley)[g] | Chlorpyrifos | 0.110 | 0.005 | 0.05 |
| | Imidacloprid | 0.0489 | 0.0024 | 0.05[c] |
| | Linuron | 1.10 | 0.05 | T1[f] |
| S4 (Green Bean) | Carbendazim | 0.181 | 0.009 | - |
| | Omethoate | 1.91 | 0.10 | 2 |
| | Pyraclostrobin | 1.11 | 0.06 | 0.6 |

[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 a number of different permitted residues.

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

[d] Sum of pirimicarb, demethyl-pirimicarb and the N-formyl-(methylamino) analogue (demethylformamido-pirimicarb).

[e] Sum of isomers.

[f] Sum of linuron plus 3,4-dichloroaniline.

[g] Sample S3 was prepared using non-organic parsley and contained additional incurred analytes.

### 2.2 Study Timetable

The timetable of the study was:

Invitations sent 30/05/2022

Samples sent 27/06/2022

Results due 8/08/2022

Interim report 10/08/2022

Due to the provision of eight reference values in this study, the release of the final report was delayed.

### 2.3 Participation and Laboratory Code

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

### 2.4 Sample Preparation

Four test samples were prepared by adding pesticide standard solutions to pureed tomatoes (Sample S1), lettuce (Sample S2), parsley (Sample S3) and green beans (Sample S4). 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.

Homogeneity testing was also conducted in this study for Samples S1, S2 and S3, and these samples were found to be sufficiently homogeneous for use in this PT study. Additionally, the

results returned by participants gave no reason to question the homogeneity 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 the analytes selected were stable in frozen fresh produce. Short-term stability testing was also conducted for Samples S1 and S2, and these samples were found to be sufficiently stable for use in this PT study. To further assess possible instability, the results returned by participants were compared to the spiked values. Robust averages of participants' results were 91% to 111% of the spiked values for Sample S1, 97% to 104% for Sample S2, 91% to 109% for Sample S3, and 72% to 95% for Sample S4. These values are similar to values observed in previous studies, and give good support for the stability of the samples. Actual transportation stability was also considered by comparing participants' results to the number of days the samples spent in transit, and there was no evidence of analyte instability.

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

### 2.6 Sample Storage and Dispatch

After preparation and prior to dispatch, the samples were stored in a freezer at approximately -20 °C. Participants were sent 100 g portions of both spiked and unspiked Samples S1, S2 and S4, 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 27 June 2022.

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 thaw and thoroughly mix the PT samples before analysis.
- 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 ± 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 25 July 2022 by email to proficiency@measurement.gov.au.

The results due date was later extended to 8 August 2022 due to customs clearance delays affecting sample delivery to some international participants.

### 2.8 Interim Report

An interim report was emailed to all participants on 10 August 2022.

## 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 were 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 | Duplicate analysis | Recoveries of SS | NMI Uncertainty Course |
| 2 | Standard deviation of replicate analyses multiplied by 2 or 3 | | Instrument calibration<br>Recoveries of SS<br>Standard purity | Eurachem/CITAC Guide |
| 3 | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS | Standard purity | Eurachem/CITAC Guide |
| 4 | Standard Operating Procedure of the laboratory | Control samples - SS<br>Duplicate analysis | Recoveries of SS | Eurachem/CITAC Guide |
| 5 | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS | Standard purity | NATA Technical Note 33 |
| 6 | Top Down - precision and estimates of the method and laboratory bias | Duplicate analysis | Recoveries of SS | NMI Uncertainty Course |
| 7 | Top Down - precision and estimates of the method and laboratory bias | Duplicate analysis<br>Instrument calibration | Instrument calibration<br>Laboratory bias from PT studies<br>Recoveries of SS<br>Standard purity | NATA Technical Note 33 |
| 8 | Top Down - reproducibility (standard deviation) from PT studies used directly | Control samples - SS<br>Duplicate analysis | Recoveries of SS | SANTE 12682/2019 |
| 9 | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS<br>Duplicate analysis | | Eurachem/CITAC Guide |
| 10 | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS | CRM<br>Recoveries of SS<br>Standard purity | ISO/GUM |
| 11 | Top Down - precision and estimates of the method and laboratory bias | Instrument calibration | Recoveries of SS | ISO/GUM |

| Lab. Code | Approach to Estimating MU | Information Sources for MU Estimation* | | Guide Document for Estimating MU |
|---|---|---|---|---|
| | | Precision | Method Bias | |
| 12 | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS | Recoveries of SS | Eurachem/CITAC Guide |
| 13 | | | | |
| 14 | Horwitz formula | Control samples<br>Duplicate analysis<br>Instrument calibration | Recoveries of SS | NMI Uncertainty Course |
| 15 | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS<br>Duplicate analysis<br>Instrument calibration | CRM<br>Instrument calibration<br>Recoveries of SS<br>Standard purity | SANTE 12682/2019 |
| 16 | Top Down - precision and estimates of the method and laboratory bias | Duplicate analysis<br>Instrument calibration | Recoveries of SS<br>Standard purity | SANTE 12682/2019 |
| 17 | Top Down - precision and estimates of the method and laboratory bias | 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 |
| 18 | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS | Laboratory bias from PT studies<br>Recoveries of SS | |
| 19 | Top Down - precision and estimates of the method and laboratory bias | Control samples<br>Duplicate analysis<br>Instrument calibration | Recoveries of SS | Eurachem/CITAC Guide |
| 20 | Bottom Up (ISO/GUM, fish bone/cause and effect diagram) | Control samples - SS | Recoveries of SS<br>Standard purity | Eurachem/CITAC Guide |

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

### 3.3 Participants' Comments

Participants were invited to make 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 were modified so that the participant cannot be identified.

Table 4 Participants' Comments

| Lab. Code | Sample | Participant's Comments | Study Coordinator's Response |
|---|---|---|---|
| 1 | S3 | Dithiocarbamates (1.7 mg/kg, +/- 0.51, 75%, by CS2 and GC-MS) and Difenoconazole (0.033 +/-0.009, 102 % rec, by LC-MSMS) were incurred value, also detected at same level in blank unspiked sample | |
| 2 | S3 | Found Linuron, Permethrin, Chlorothalonil and Difenconazole in unspiked sample. | |
| 4 | S3 and S4 | No detected analytes | |

| Lab. Code | Sample | Participant's Comments | Study Coordinator's Response |
|---|---|---|---|
| 7 | S3 | Chlorothalonil and Permethrin were detected on both spiked and unspiked sample. Linuron was reported as sum of sum of Linuron plus 3,4-dichloroaniline | |
| 8 | S3 | Sample blank detected Permethrin 0.0854 mg/kg | |
| 9 | S3 | Nearly same level concentration of Dithiocarbamates and Permethrin is found in both spiked and unspiked sample. | |
| 10 | S3 | Small positives for Chlorothalonil and Difenoconazole in both spiked and unspiked, not reported above | |
| 11 | S1 | AMPA detected in sample S1 at 0.05mg/kg, and sample S1 unspiked at 0.03mg/kg. | |
| | S3 | Permethrin found in sample S3 unspiked at 0.11 mg/kg. Difenconazole found in sample S3 and sample S3 unspiked at 0.03mg/kg. Metalaxyl found in sample S3 and sample S3 unspiked at 0.005mg/kg | |
| 14 | S1 | Note trace Azoxystrobin also present in BLKS1. | |
| | S2 | Note trace spinosad level also present in BLKS2. | |
| | S3 | Note Difenoconazole and Permethrin are present in BLK S3, and there is also a trace level of Chlorthal Dimethyl (<0.01) present in sample and BLKS3 | |
| 15 | S1 | The concentration of pesticides reported is an average of five 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. | |
| | S2 and S3 | The concentration of pesticides reported is an average of three 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. | |
| | S4 | No pesticides were detected at or above the Limit of Quantitation (LOQ) at 0.01 mg/kg after five determinations made on the same sample. The unspiked sample was also analysed and found to have no residues at or above the LOQ. | |
| | All | This PT is important for the reliability and assessment of our laboratory's results, and also for compliance to ISO/IEC 17025 accreditation. We would like to suggest PT studies for pesticide residues in other sample matrices such as rice, banana, pineapple, mango and water.<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 suggestions.<br>This year we have introduced a pesticides in potable water PT study, and we also already run an annual pesticides in river water PT study. We will take into consideration the other matrix suggestions for future PT studies. |

# 4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

## 4.1 Results Summary

Participant results are listed in Tables 5 to 21 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). Bar charts of results and performance scores are presented in Figures 2 to 18. An example chart with interpretation guide is shown in Figure 1.

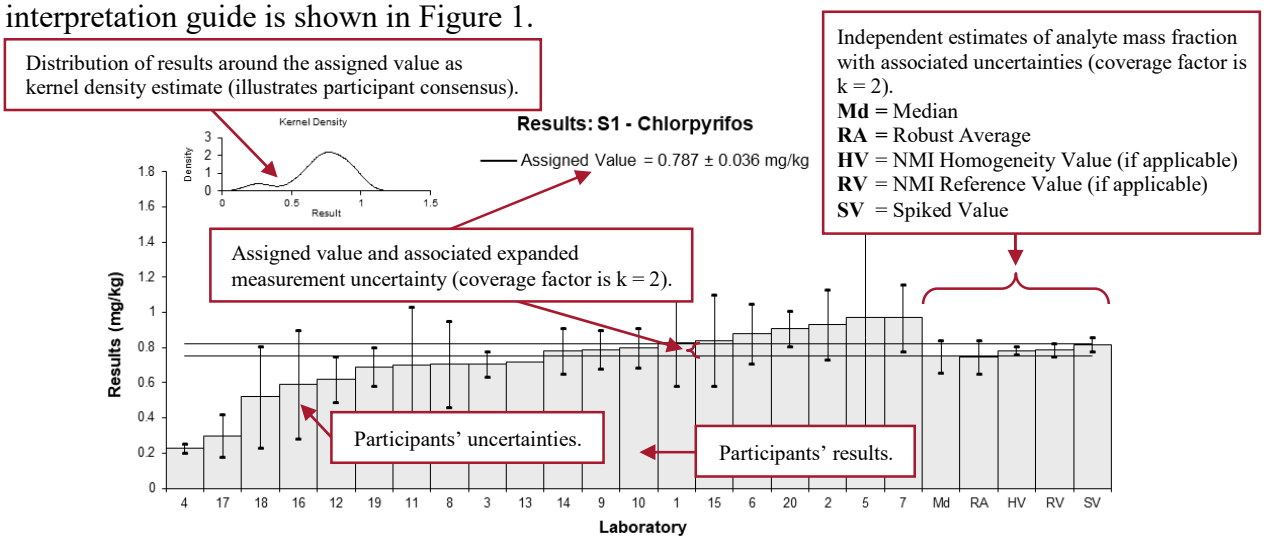



Figure 1 Guide to Presentation of Results

## 4.2 Outliers and Gross Errors

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] Gross errors were obvious blunders, e.g. results reported with incorrect units or for a different analyte or sample, and such results were removed for the calculation of all summary statistics.[3,4]

## 4.3 Assigned Value

The assigned value is defined as the 'value attributed to a particular property of a proficiency test item'.[1] In this PT study, this property is the mass fraction of the analytes in the samples. The assigned values for Sample S1 bifenthrin, buprofezin, chlorpyrifos, endosulfan sulfate, imazalil and pirimicarb, and Sample S2 endosulfan sulfate and pirimicarb, were reference values as determined by isotope dilution mass spectrometry (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 13528:2022.[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.

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

### 4.8 $E_n$ Score

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

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

where:

$E_n$ is $E_n$ score

$\chi$ is a participant's result

$X$ is the assigned value

$U_\chi$ is the expanded measurement uncertainty of the participant's result

$U_X$ is the expanded measurement uncertainty of the assigned value

For the absolute value of an $E_n$ score:

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

### 4.9 Traceability and Measurement Uncertainty

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

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

## 5 TABLES AND FIGURES

Table 5

**Sample Details**

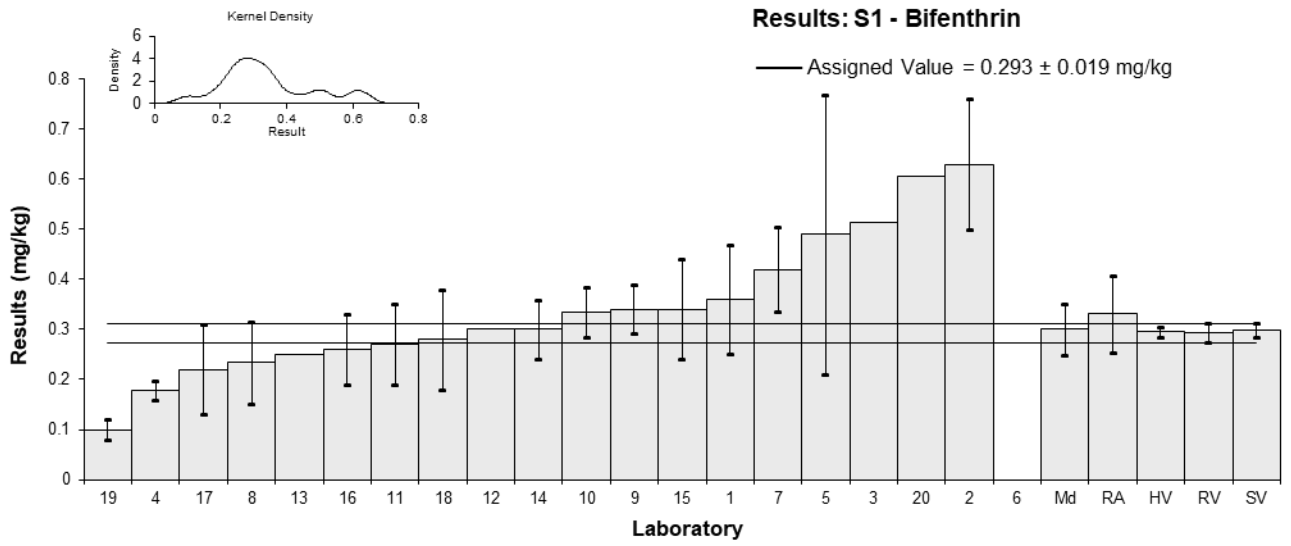
| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Tomato |
| **Analyte** | Bifenthrin |
| **Unit** | mg/kg |

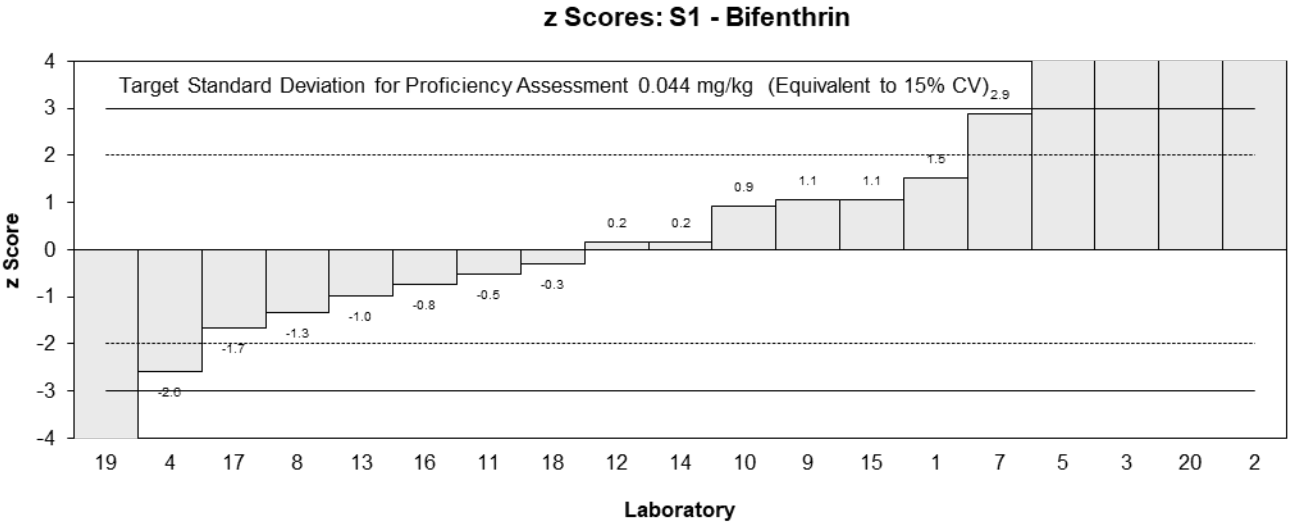
**Participant Results**

| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.36 | 0.11 | 94 | 1.52 | 0.60 |
| **2** | 0.63 | 0.13 | 68 | 7.67 | 2.57 |
| **3** | 0.513 | NR | 82.17 | 5.01 | 11.58 |
| **4** | 0.179 | 0.019 | NR | -2.59 | -4.24 |
| **5** | 0.49 | 0.28 | 75 | 4.48 | 0.70 |
| **6** | NT | NT | NT | | |
| **7** | 0.42 | 0.085 | 86 | 2.89 | 1.46 |
| **8** | 0.234 | 0.082 | 84 | -1.34 | -0.70 |
| **9** | 0.34 | 0.049 | 86 | 1.07 | 0.89 |
| **10** | 0.334 | 0.05 | 92 | 0.93 | 0.77 |
| **11** | 0.27 | 0.081 | 87 | -0.52 | -0.28 |
| **12** | 0.30 | NR | 99 | 0.16 | 0.37 |
| **13** | 0.25 | NR | NR | -0.98 | -2.26 |
| **14** | 0.3 | 0.06 | 94 | 0.16 | 0.11 |
| **15** | 0.34 | 0.10 | 51 | 1.07 | 0.46 |
| **16** | 0.26 | 0.07 | 83 | -0.75 | -0.45 |
| **17** | 0.22 | 0.09 | 72 | -1.66 | -0.79 |
| **18** | 0.28 | 0.10 | 97 | -0.30 | -0.13 |
| **19** | 0.1 | 0.02 | 100 | -4.39 | -7.00 |
| **20** | 0.605 | NR | 160 | 7.10 | 16.42 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.293 | 0.019 |
| **Spike Value** | 0.299 | 0.015 |
| **Homogeneity Value** | 0.295 | 0.010 |
| **Reference Value** | 0.293 | 0.019 |
| **Robust Average** | 0.331 | 0.077 |
| **Median** | 0.300 | 0.051 |
| **Mean** | 0.338 | |
| **N** | 19 | |
| **Max** | 0.63 | |
| **Min** | 0.1 | |
| **Robust SD** | 0.13 | |
| **Robust CV** | 41% | |


Kernel Density
Density
Result
Results: S1 - Bifenthrin
Assigned Value = 0.293 ± 0.019 mg/kg
Results (mg/kg)
Laboratory
19 4 17 8 13 16 11 18 12 14 10 9 15 1 7 5 3 20 2 6 Md RA HV RV SV


z Scores: S1 - Bifenthrin
Target Standard Deviation for Proficiency Assessment 0.044 mg/kg (Equivalent to 15% CV)2.9
z Score
Laboratory
19 4 17 8 13 16 11 18 12 14 10 9 15 1 7 5 3 20 2

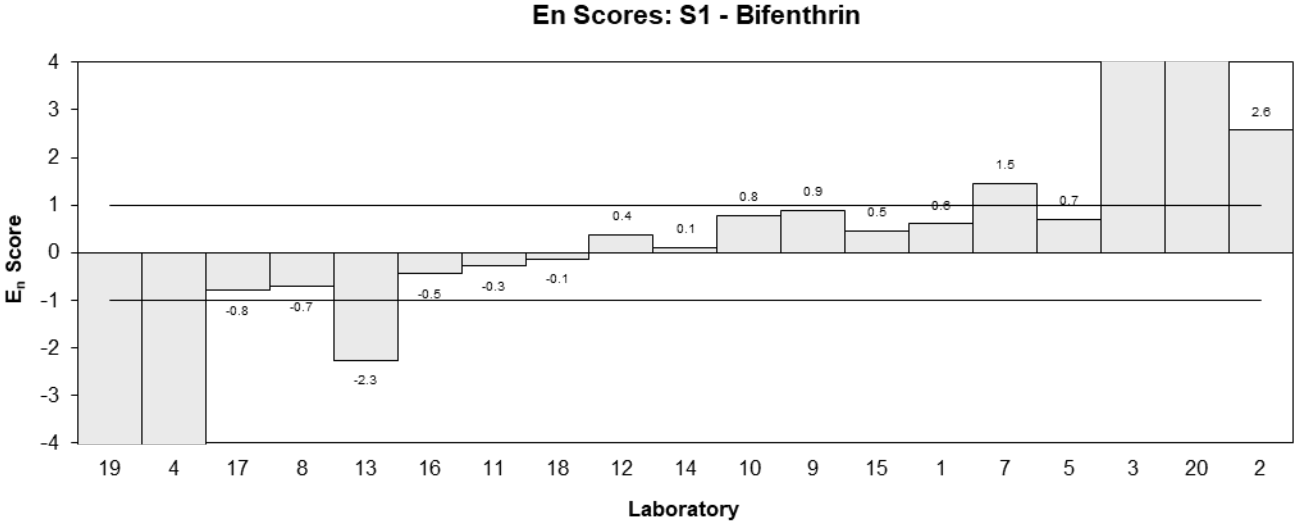

En Scores: S1 - Bifenthrin
En Score
Laboratory
19 4 17 8 13 16 11 18 12 14 10 9 15 1 7 5 3 20 2

Figure 2

Table 6

**Sample Details**

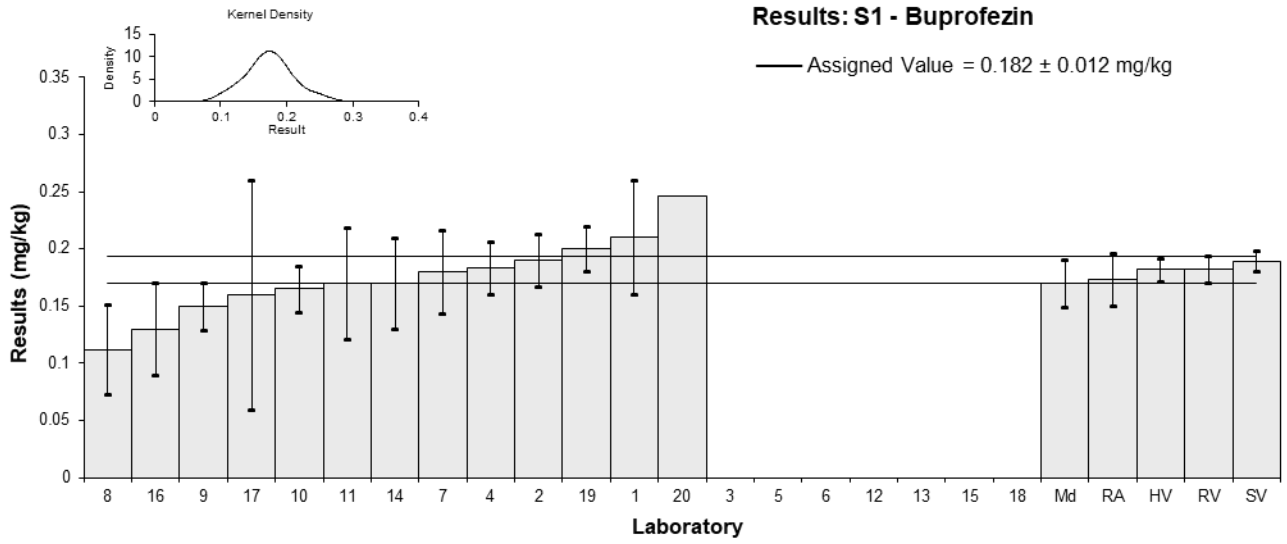
| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Tomato |
| **Analyte** | Buprofezin |
| **Unit** | mg/kg |

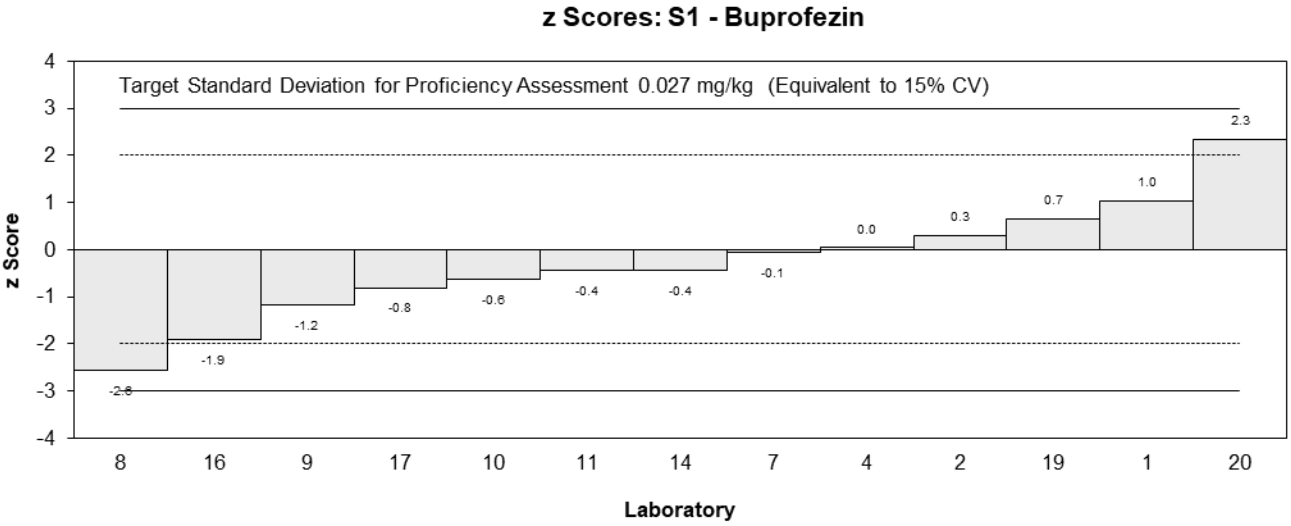
**Participant Results**

| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.21 | 0.05 | 113 | 1.03 | 0.54 |
| **2** | 0.19 | 0.023 | 80 | 0.29 | 0.31 |
| **3** | NT | NT | NT | | |
| **4** | 0.183 | 0.023 | NR | 0.04 | 0.04 |
| **5** | NT | NT | NT | | |
| **6** | NT | NT | NT | | |
| **7** | 0.18 | 0.036 | 95 | -0.07 | -0.05 |
| **8** | 0.112 | 0.039 | 95 | -2.56 | -1.72 |
| **9** | 0.15 | 0.021 | 87 | -1.17 | -1.32 |
| **10** | 0.165 | 0.02 | 81 | -0.62 | -0.73 |
| **11** | 0.17 | 0.049 | 89 | -0.44 | -0.24 |
| **12** | NT | NT | NT | | |
| **13** | NR | NR | NR | | |
| **14** | 0.17 | 0.04 | 95 | -0.44 | -0.29 |
| **15** | NT | NT | NT | | |
| **16** | 0.13 | 0.04 | 63 | -1.90 | -1.25 |
| **17** | 0.16 | 0.10 | 90 | -0.81 | -0.22 |
| **18** | NT | NT | NT | | |
| **19** | 0.2 | 0.02 | 86.1 | 0.66 | 0.77 |
| **20** | 0.246 | NR | 94 | 2.34 | 5.33 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.182 | 0.012 |
| **Spike Value** | 0.189 | 0.009 |
| **Homogeneity Value** | 0.182 | 0.010 |
| **Reference Value** | 0.182 | 0.012 |
| **Robust Average** | 0.173 | 0.023 |
| **Median** | 0.170 | 0.021 |
| **Mean** | 0.174 | |
| **N** | 13 | |
| **Max** | 0.246 | |
| **Min** | 0.112 | |
| **Robust SD** | 0.033 | |
| **Robust CV** | 19% | |


Kernel Density
Density
Result
Results: S1 - Buprofezin
Assigned Value = 0.182 ± 0.012 mg/kg
Results (mg/kg)
Laboratory
8 16 9 17 10 11 14 7 4 2 19 1 20 3 5 6 12 13 15 18 Md RA HV RV SV


z Scores: S1 - Buprofezin
Target Standard Deviation for Proficiency Assessment 0.027 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
8 16 9 17 10 11 14 7 4 2 19 1 20
-2.6 -1.9 -1.2 -0.8 -0.6 -0.4 -0.4 -0.1 0.0 0.3 0.7 1.0 2.3

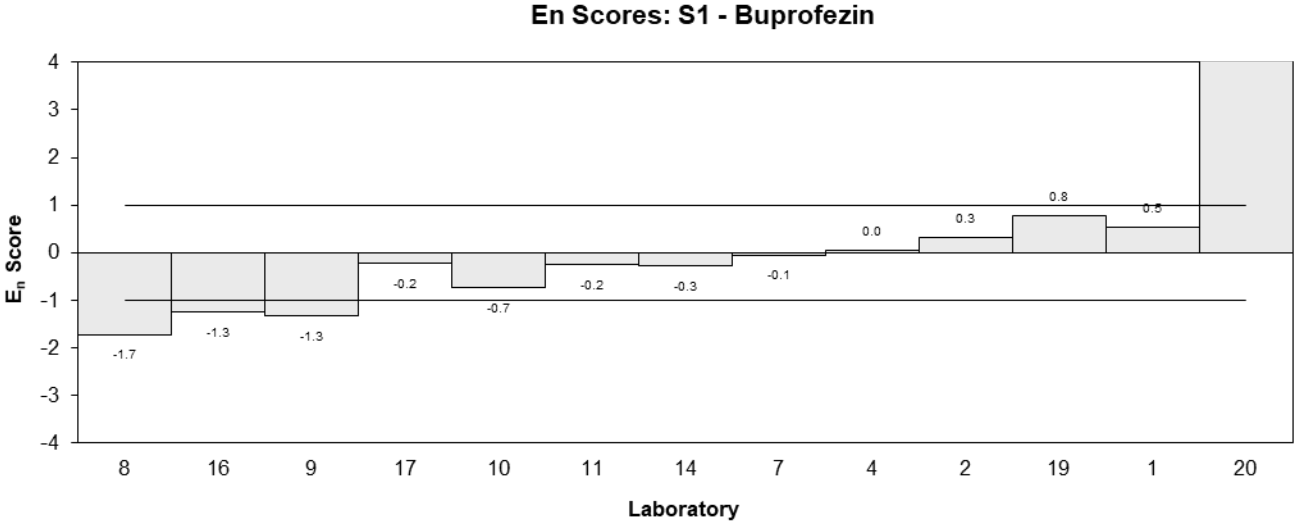

En Scores: S1 - Buprofezin
En Score
Laboratory
8 16 9 17 10 11 14 7 4 2 19 1 20
-1.7 -1.3 -1.3 -0.2 -0.7 -0.2 -0.3 -0.1 0.0 0.3 0.8 0.5

Figure 3

Table 7

**Sample Details**

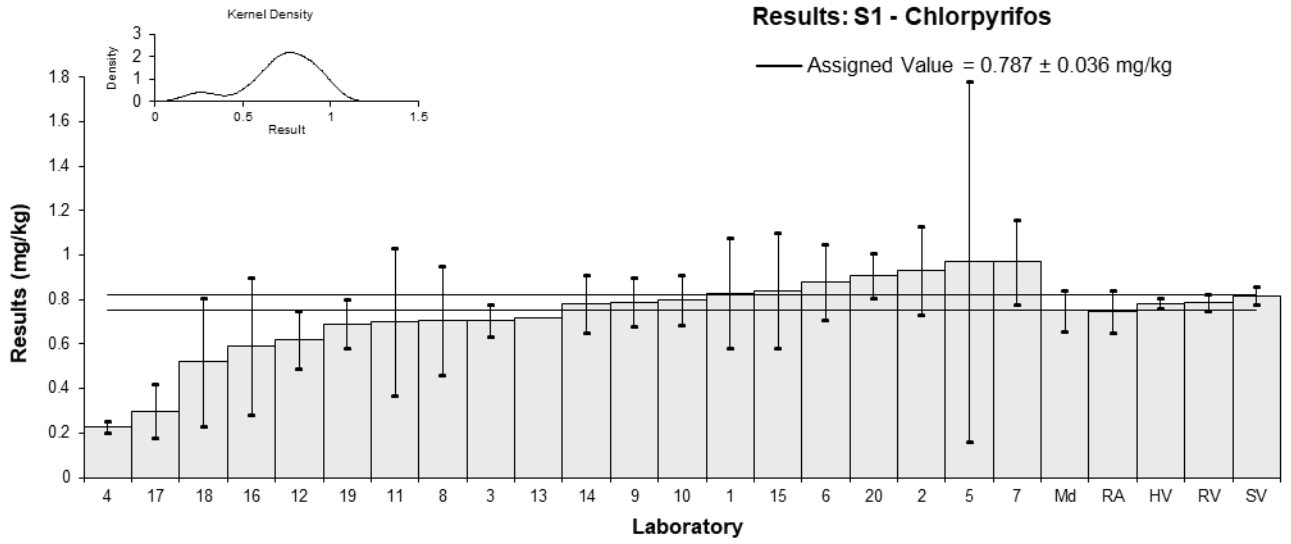
| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Tomato |
| **Analyte** | Chlorpyrifos |
| **Unit** | mg/kg |

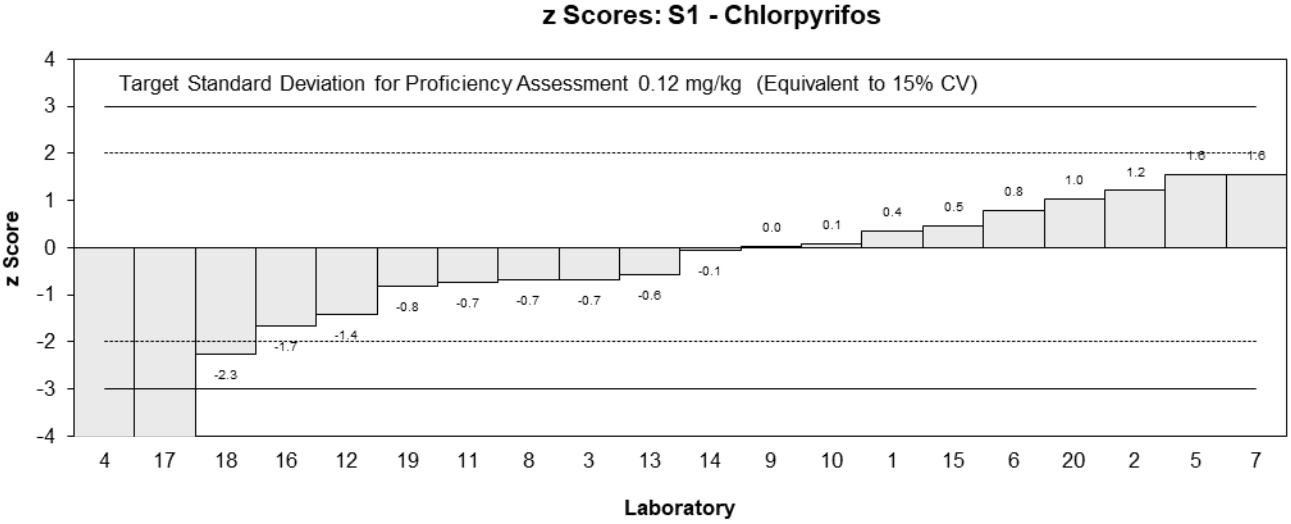
**Participant Results**

| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.83 | 0.25 | 75 | 0.36 | 0.17 |
| **2** | 0.93 | 0.2 | 105 | 1.21 | 0.70 |
| **3** | 0.707 | 0.073 | 85.67 | -0.68 | -0.98 |
| **4** | 0.226 | 0.026 | NR | -4.75 | -12.63 |
| **5** | 0.97 | 0.81 | 64 | 1.55 | 0.23 |
| **6** | 0.88 | 0.17 | NR | 0.79 | 0.54 |
| **7** | 0.97 | 0.19 | 100 | 1.55 | 0.95 |
| **8** | 0.706 | 0.247 | 88 | -0.69 | -0.32 |
| **9** | 0.79 | 0.11 | 79 | 0.03 | 0.03 |
| **10** | 0.797 | 0.112 | 104 | 0.08 | 0.09 |
| **11** | 0.70 | 0.33 | 80 | -0.74 | -0.26 |
| **12** | 0.62 | 0.13 | 78 | -1.41 | -1.24 |
| **13** | 0.72 | NR | NR | -0.57 | -1.86 |
| **14** | 0.78 | 0.13 | 95 | -0.06 | -0.05 |
| **15** | 0.84 | 0.26 | 87 | 0.45 | 0.20 |
| **16** | 0.59 | 0.31 | 90 | -1.67 | -0.63 |
| **17** | 0.30 | 0.12 | 108 | -4.13 | -3.89 |
| **18** | 0.52 | 0.29 | 41 | -2.26 | -0.91 |
| **19** | 0.69 | 0.11 | 90.3 | -0.82 | -0.84 |
| **20** | 0.909 | 0.102 | 86 | 1.03 | 1.13 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.787 | 0.036 |
| **Spike Value** | 0.819 | 0.041 |
| **Homogeneity Value** | 0.784 | 0.023 |
| **Reference Value** | 0.787 | 0.036 |
| **Robust Average** | 0.747 | 0.095 |
| **Median** | 0.750 | 0.091 |
| **Mean** | 0.724 | |
| **N** | 20 | |
| **Max** | 0.97 | |
| **Min** | 0.226 | |
| **Robust SD** | 0.17 | |
| **Robust CV** | 23% | |


Kernel Density
Density
Result
Results: S1 - Chlorpyrifos
Assigned Value = 0.787 ± 0.036 mg/kg
Results (mg/kg)
Laboratory
4 17 18 16 12 19 11 8 3 13 14 9 10 1 15 6 20 2 5 7 Md RA HV RV SV


z Scores: S1 - Chlorpyrifos
Target Standard Deviation for Proficiency Assessment 0.12 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
4 17 18 16 12 19 11 8 3 13 14 9 10 1 15 6 20 2 5 7
-2.3 -1.7 -1.4 -0.8 -0.7 -0.7 -0.7 -0.6 -0.1 0.0 0.1 0.4 0.5 0.8 1.0 1.2 1.6 1.6

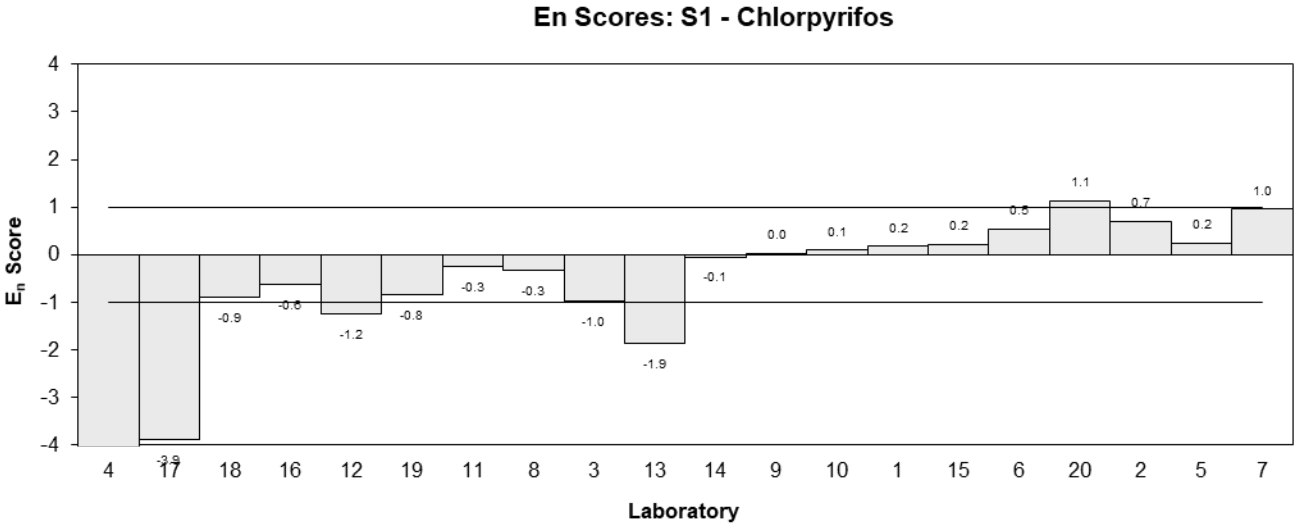

En Scores: S1 - Chlorpyrifos
En Score
Laboratory
4 17 18 16 12 19 11 8 3 13 14 9 10 1 15 6 20 2 5 7
-3.9 -0.9 -0.6 -1.2 -0.8 -0.3 -0.3 -1.0 -1.9 -0.1 0.0 0.1 0.2 0.2 0.5 1.1 0.7 0.2 1.0

Figure 4

Table 8

**Sample Details**

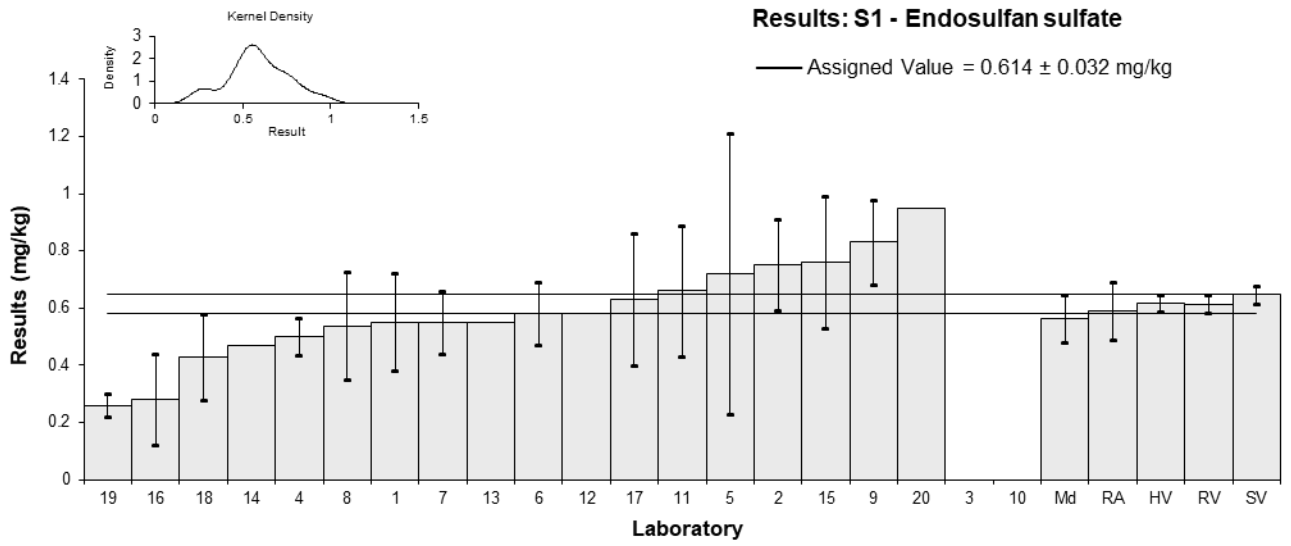
| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Tomato |
| **Analyte** | Endosulfan sulfate |
| **Unit** | mg/kg |

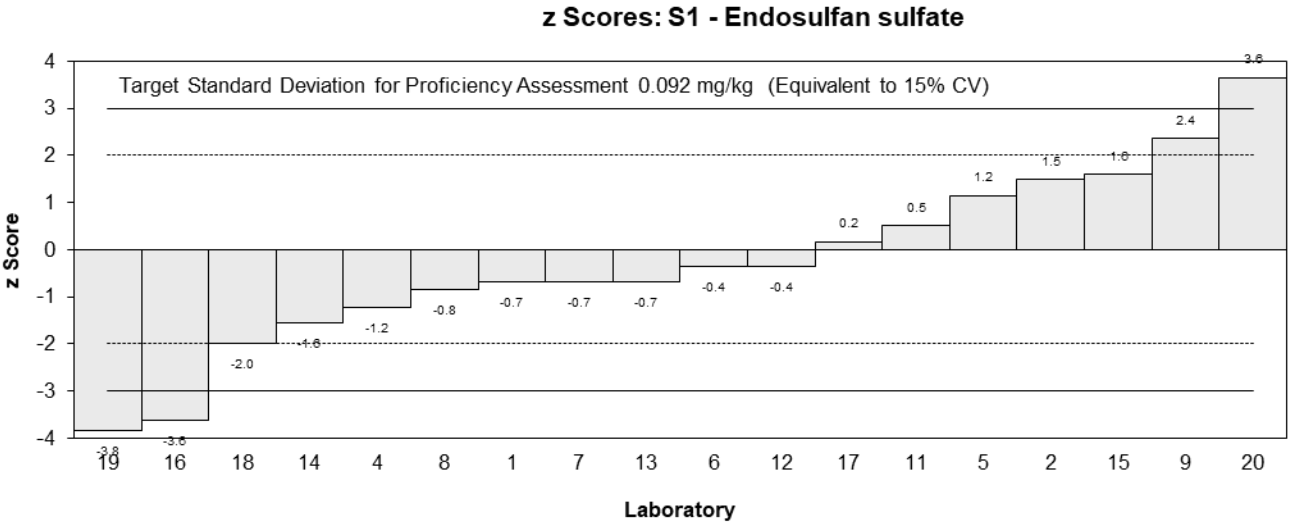
**Participant Results**

| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.55 | 0.17 | 88 | -0.69 | -0.37 |
| **2** | 0.75 | 0.16 | 99 | 1.48 | 0.83 |
| **3** | NR | NR | NR | | |
| **4** | 0.501 | 0.065 | NR | -1.23 | -1.56 |
| **5** | 0.72 | 0.49 | 88 | 1.15 | 0.22 |
| **6** | 0.58 | 0.11 | NR | -0.37 | -0.30 |
| **7** | 0.55 | 0.11 | 97 | -0.69 | -0.56 |
| **8** | 0.537 | 0.188 | 84 | -0.84 | -0.40 |
| **9** | 0.83 | 0.15 | 96 | 2.35 | 1.41 |
| **10** | NT | NT | NT | | |
| **11** | 0.66 | 0.23 | 102 | 0.50 | 0.20 |
| **12** | 0.58 | NR | 105 | -0.37 | -1.06 |
| **13** | 0.55 | NR | NR | -0.69 | -2.00 |
| **14** | 0.47 | NR | 100 | -1.56 | -4.50 |
| **15** | 0.76 | 0.23 | 39 | 1.59 | 0.63 |
| **16** | 0.28 | 0.16 | 104 | -3.63 | -2.05 |
| **17** | 0.63 | 0.23 | 88 | 0.17 | 0.07 |
| **18** | 0.43 | 0.15 | 99 | -2.00 | -1.20 |
| **19** | 0.26 | 0.04 | 97 | -3.84 | -6.91 |
| **20** | 0.949 | NR | 85 | 3.64 | 10.47 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.614 | 0.032 |
| **Spike Value** | 0.647 | 0.032 |
| **Homogeneity Value** | 0.616 | 0.028 |
| **Reference Value** | 0.614 | 0.032 |
| **Robust Average** | 0.59 | 0.10 |
| **Median** | 0.565 | 0.083 |
| **Mean** | 0.588 | |
| **N** | 18 | |
| **Max** | 0.949 | |
| **Min** | 0.26 | |
| **Robust SD** | 0.17 | |
| **Robust CV** | 29% | |


Kernel Density
Density
Result
Results: S1 - Endosulfan sulfate
Assigned Value = 0.614 ± 0.032 mg/kg
Results (mg/kg)
Laboratory
19 16 18 14 4 8 1 7 13 6 12 17 11 5 2 15 9 20 3 10 Md RA HV RV SV


z Scores: S1 - Endosulfan sulfate
Target Standard Deviation for Proficiency Assessment 0.092 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
19 16 18 14 4 8 1 7 13 6 12 17 11 5 2 15 9 20

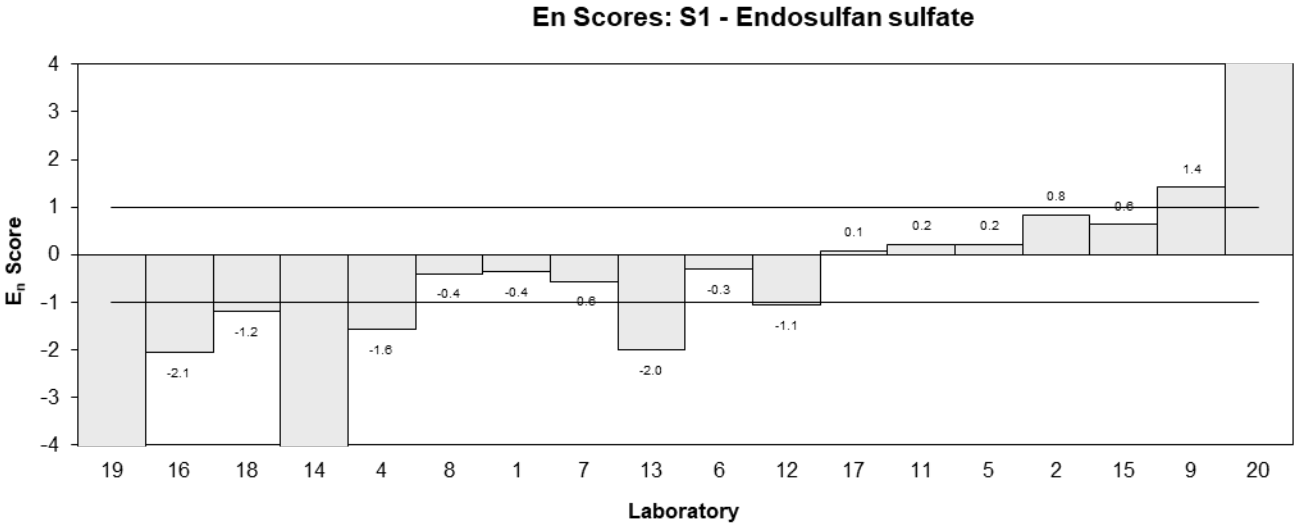

En Scores: S1 - Endosulfan sulfate
En Score
Laboratory
19 16 18 14 4 8 1 7 13 6 12 17 11 5 2 15 9 20

Figure 5

Table 9

**Sample Details**

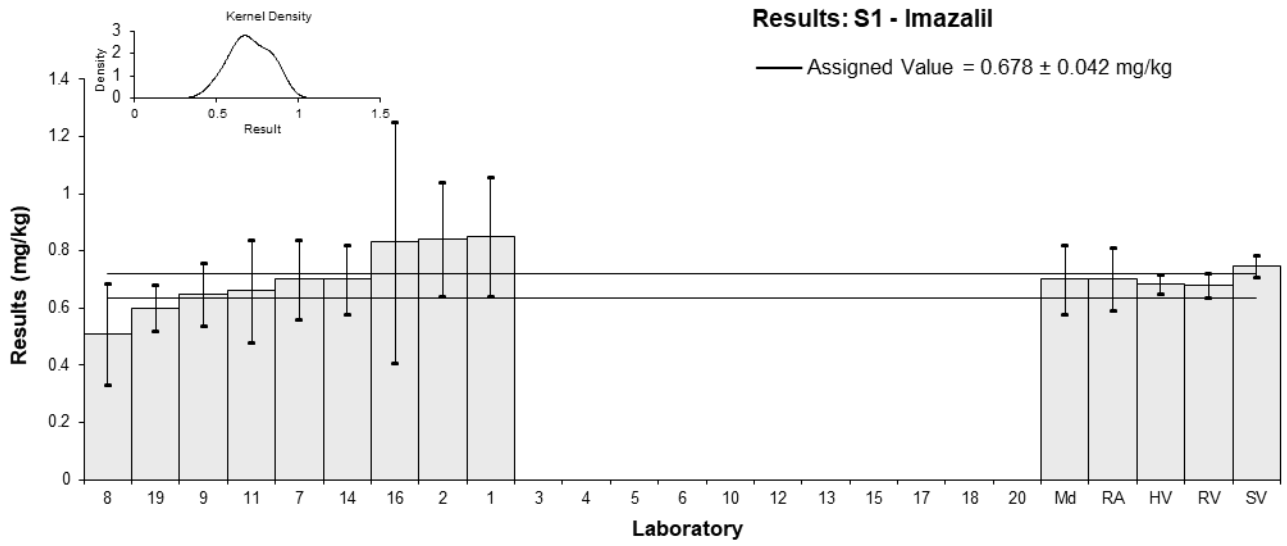
| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Tomato |
| **Analyte** | Imazalil |
| **Unit** | mg/kg |

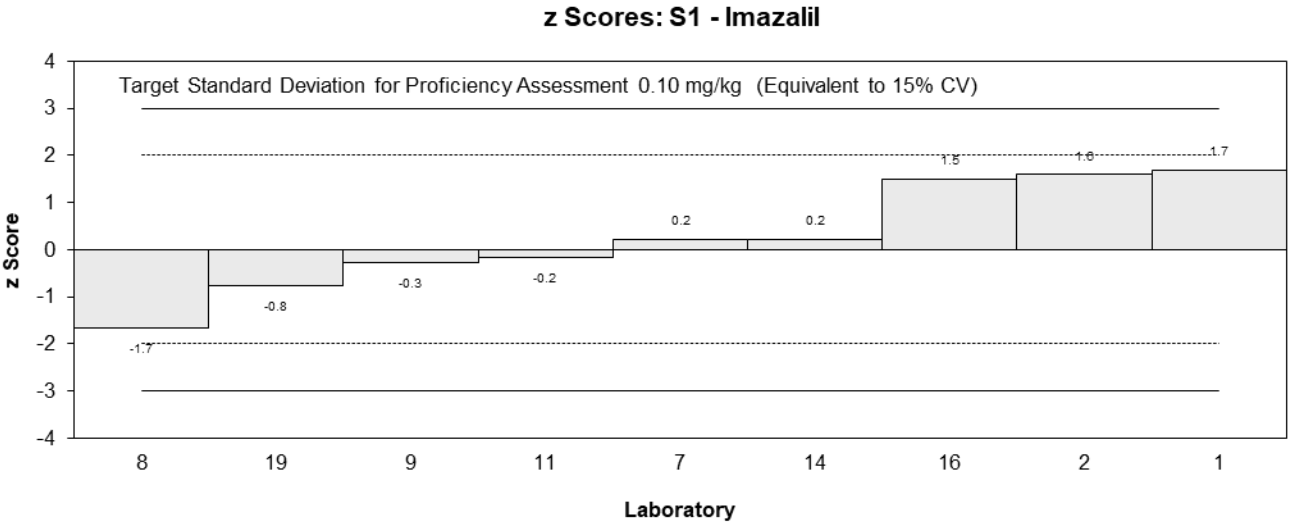
**Participant Results**

| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.85 | 0.21 | 96 | 1.69 | 0.80 |
| **2** | 0.84 | 0.2 | 87 | 1.59 | 0.79 |
| **3** | NT | NT | NT | | |
| **4** | NT | NT | NT | | |
| **5** | NT | NT | NT | | |
| **6** | NT | NT | NT | | |
| **7** | 0.70 | 0.14 | 85 | 0.22 | 0.15 |
| **8** | 0.509 | 0.178 | 83 | -1.66 | -0.92 |
| **9** | 0.65 | 0.11 | 76 | -0.28 | -0.24 |
| **10** | NT | NT | NT | | |
| **11** | 0.66 | 0.18 | 90 | -0.18 | -0.10 |
| **12** | NT | NT | NT | | |
| **13** | NR | NR | NR | | |
| **14** | 0.70 | 0.12 | 100 | 0.22 | 0.17 |
| **15** | NT | NT | NT | | |
| **16** | 0.83 | 0.42 | 104 | 1.49 | 0.36 |
| **17** | NT | NT | NT | | |
| **18** | NT | NT | NT | | |
| **19** | 0.6 | 0.08 | 96.5 | -0.77 | -0.86 |
| **20** | NT | NT | NT | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.678 | 0.042 |
| **Spike Value** | 0.746 | 0.037 |
| **Homogeneity Value** | 0.684 | 0.033 |
| **Reference Value** | 0.678 | 0.042 |
| **Robust Average** | 0.70 | 0.11 |
| **Median** | 0.70 | 0.12 |
| **Mean** | 0.704 | |
| **N** | 9 | |
| **Max** | 0.85 | |
| **Min** | 0.509 | |
| **Robust SD** | 0.13 | |
| **Robust CV** | 19% | |


Kernel Density
Density
Result
Results: S1 - Imazalil
Assigned Value = 0.678 ± 0.042 mg/kg
Results (mg/kg)
Laboratory
8 19 9 11 7 14 16 2 1 3 4 5 6 10 12 13 15 17 18 20 Md RA HV RV SV


z Scores: S1 - Imazalil
Target Standard Deviation for Proficiency Assessment 0.10 mg/kg (Equivalent to 15% CV)
z Score
-1.7
-0.8
-0.3
-0.2
0.2
0.2
1.5
1.6
1.7
Laboratory
8 19 9 11 7 14 16 2 1

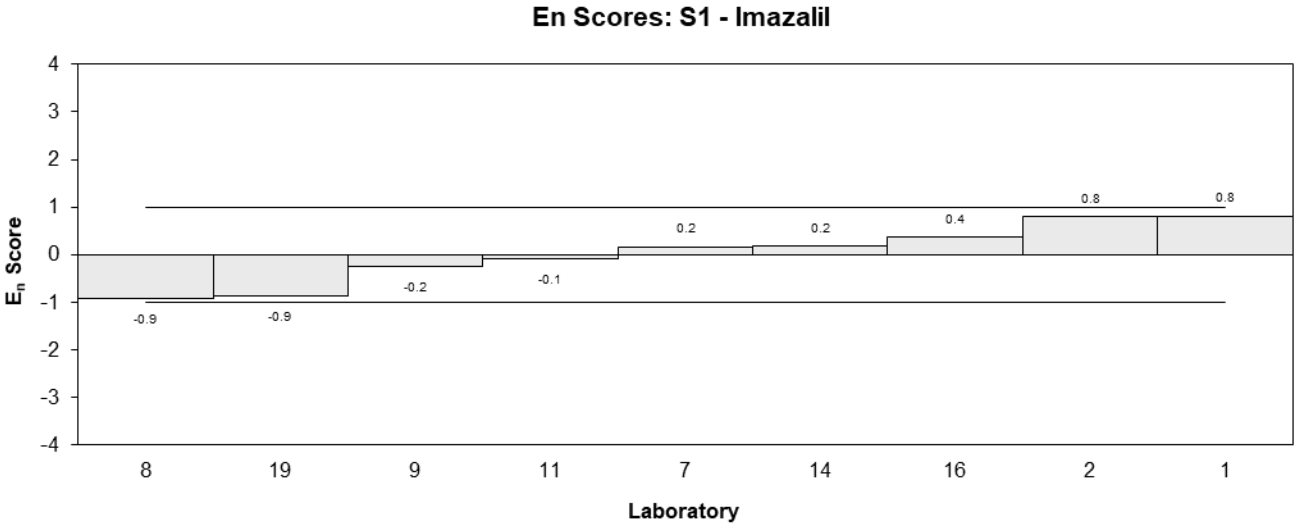

En Scores: S1 - Imazalil
En Score
-0.9
-0.9
-0.2
-0.1
0.2
0.2
0.4
0.8
0.8
Laboratory
8 19 9 11 7 14 16 2 1

Figure 6

Table 10

**Sample Details**

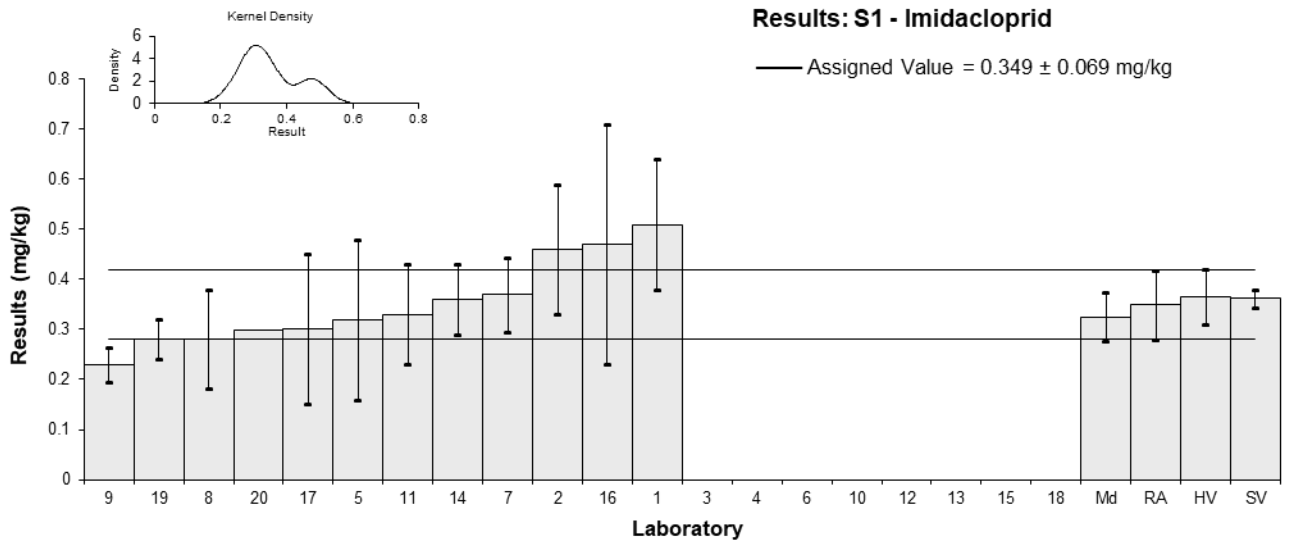
| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Tomato |
| **Analyte** | Imidacloprid |
| **Unit** | mg/kg |

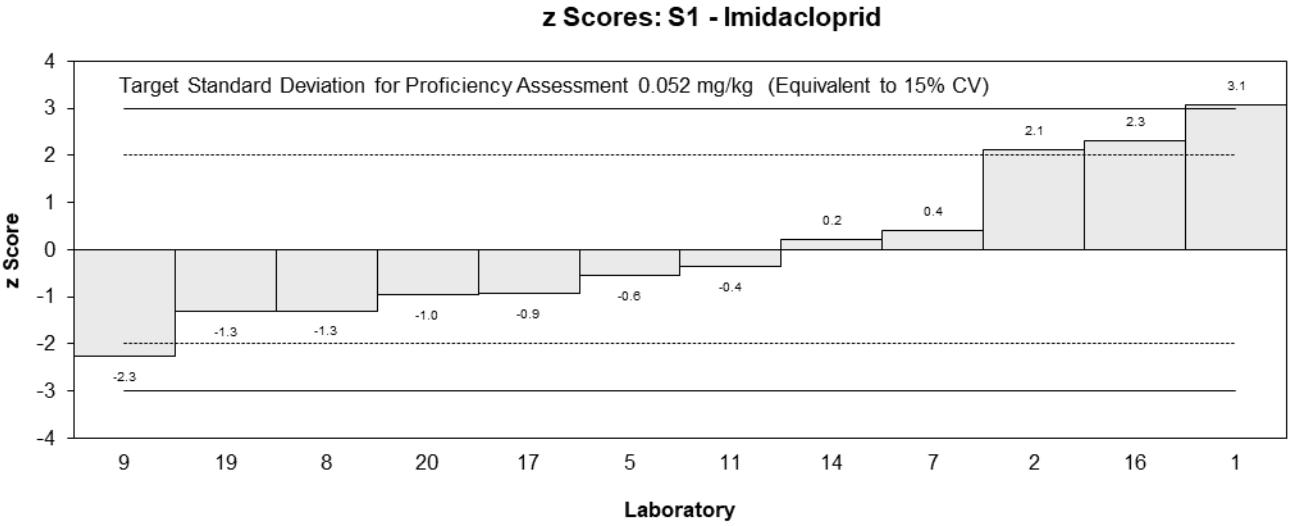
**Participant Results**

| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.51 | 0.13 | 100 | 3.08 | 1.09 |
| **2** | 0.46 | 0.13 | 102 | 2.12 | 0.75 |
| **3** | NT | NT | NT | | |
| **4** | NT | NT | NT | | |
| **5** | 0.32 | 0.16 | 75 | -0.55 | -0.17 |
| **6** | NT | NT | NT | | |
| **7** | 0.37 | 0.074 | 82 | 0.40 | 0.21 |
| **8** | 0.281 | 0.098 | 91 | -1.30 | -0.57 |
| **9** | 0.23 | 0.035 | 71 | -2.27 | -1.54 |
| **10** | NT | NT | NT | | |
| **11** | 0.33 | 0.10 | 73 | -0.36 | -0.16 |
| **12** | NT | NT | NT | | |
| **13** | NR | NR | NR | | |
| **14** | 0.36 | 0.07 | 95 | 0.21 | 0.11 |
| **15** | NT | NT | NT | | |
| **16** | 0.47 | 0.24 | 100 | 2.31 | 0.48 |
| **17** | 0.30 | 0.15 | 45 | -0.94 | -0.30 |
| **18** | NT | NT | NT | | |
| **19** | 0.28 | 0.04 | 95.8 | -1.32 | -0.87 |
| **20** | 0.299 | NR | 72 | -0.96 | -0.72 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.349 | 0.069 |
| **Spike Value** | 0.362 | 0.018 |
| **Homogeneity Value** | 0.366 | 0.055 |
| **Robust Average** | 0.349 | 0.069 |
| **Median** | 0.325 | 0.048 |
| **Mean** | 0.351 | |
| **N** | 12 | |
| **Max** | 0.51 | |
| **Min** | 0.23 | |
| **Robust SD** | 0.095 | |
| **Robust CV** | 27% | |


Kernel Density
Density
Result
Results: S1 - Imidacloprid
Assigned Value = 0.349 ± 0.069 mg/kg
Results (mg/kg)
Laboratory
9 19 8 20 17 5 11 14 7 2 16 1 3 4 6 10 12 13 15 18 Md RA HV SV


z Scores: S1 - Imidacloprid
Target Standard Deviation for Proficiency Assessment 0.052 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
9 19 8 20 17 5 11 14 7 2 16 1
-2.3 -1.3 -1.3 -1.0 -0.9 -0.6 -0.4 0.2 0.4 2.1 2.3 3.1

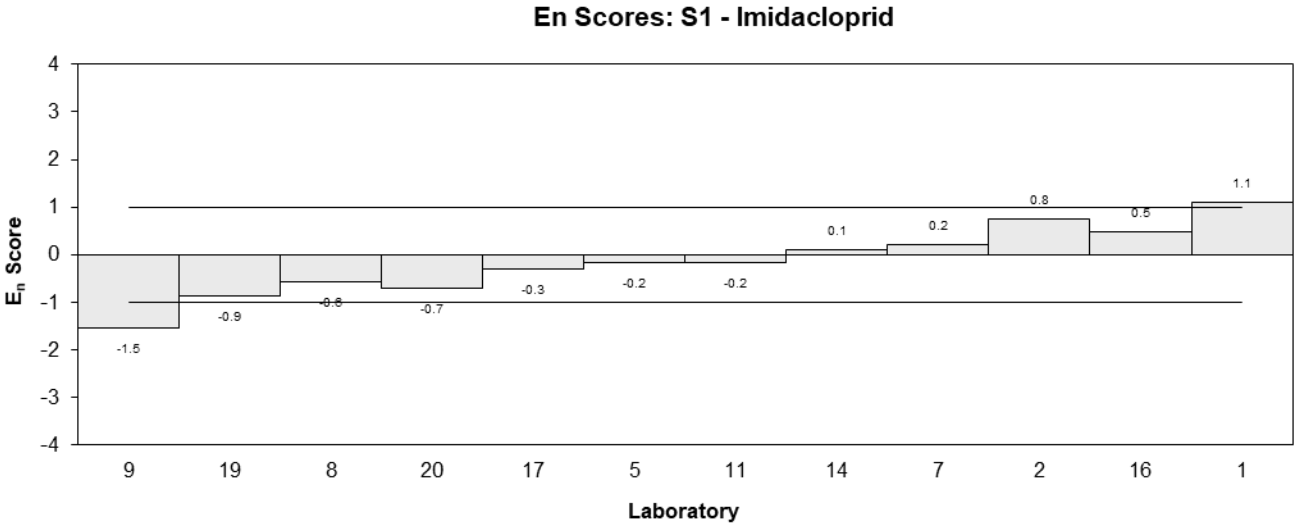

En Scores: S1 - Imidacloprid
En Score
Laboratory
9 19 8 20 17 5 11 14 7 2 16 1
-1.5 -0.9 -0.6 -0.7 -0.3 -0.2 -0.2 0.1 0.2 0.8 0.5 1.1

Figure 7

Table 11

**Sample Details**

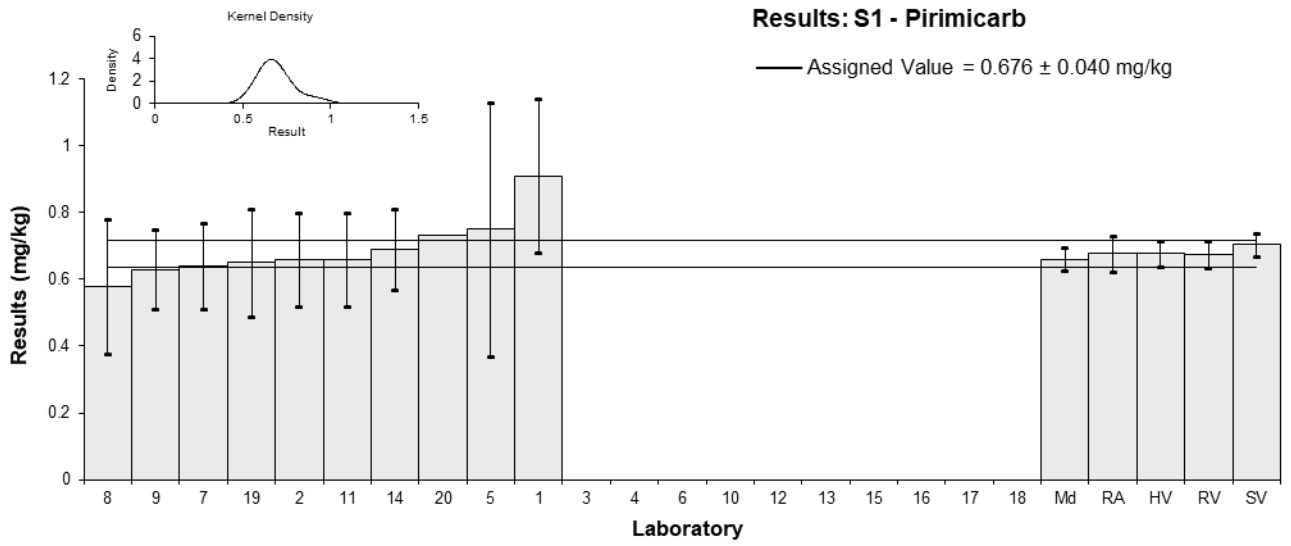
| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Tomato |
| **Analyte** | Pirimicarb |
| **Unit** | mg/kg |

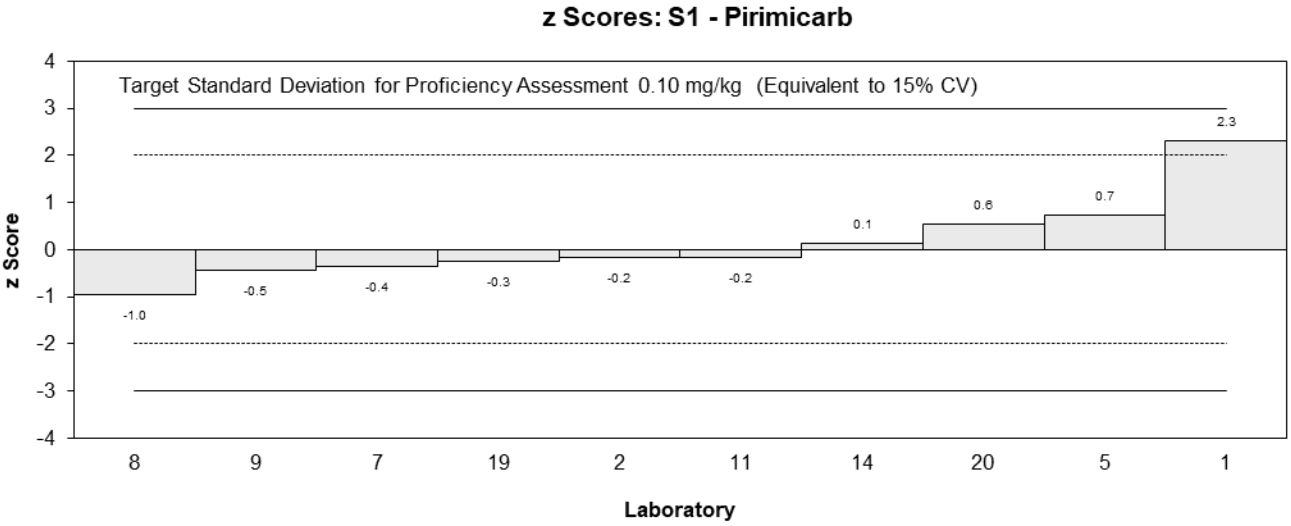
**Participant Results**

| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.91 | 0.23 | 118 | 2.31 | 1.00 |
| **2** | 0.66 | 0.14 | 80 | -0.16 | -0.11 |
| **3** | NT | NT | NT | | |
| **4** | NT | NT | NT | | |
| **5** | 0.75 | 0.38 | 115 | 0.73 | 0.19 |
| **6** | NT | NT | NT | | |
| **7** | 0.64 | 0.13 | 88 | -0.36 | -0.26 |
| **8** | 0.579 | 0.203 | 94 | -0.96 | -0.47 |
| **9** | 0.63 | 0.12 | 94 | -0.45 | -0.36 |
| **10** | NT | NT | NT | | |
| **11** | 0.66 | 0.14 | 95 | -0.16 | -0.11 |
| **12** | NT | NT | NT | | |
| **13** | NR | NR | NR | | |
| **14** | 0.69 | 0.12 | 95 | 0.14 | 0.11 |
| **15** | NT | NT | NT | | |
| **16** | NT | NT | NT | | |
| **17** | NT | NT | NT | | |
| **18** | NT | NT | NT | | |
| **19** | 0.65 | 0.16 | 82.2 | -0.26 | -0.16 |
| **20** | 0.732 | NR | 94 | 0.55 | 1.40 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.676 | 0.040 |
| **Spike Value** | 0.704 | 0.035 |
| **Homogeneity Value** | 0.678 | 0.038 |
| **Reference Value** | 0.676 | 0.040 |
| **Robust Average** | 0.677 | 0.055 |
| **Median** | 0.660 | 0.035 |
| **Mean** | 0.690 | |
| **N** | 10 | |
| **Max** | 0.91 | |
| **Min** | 0.579 | |
| **Robust SD** | 0.070 | |
| **Robust CV** | 10% | |


Kernel Density
Density
Result
Results: S1 - Pirimicarb
Assigned Value = 0.676 ± 0.040 mg/kg
Results (mg/kg)
Laboratory
8 9 7 19 2 11 14 20 5 1 3 4 6 10 12 13 15 16 17 18 Md RA HV RV SV


z Scores: S1 - Pirimicarb
Target Standard Deviation for Proficiency Assessment 0.10 mg/kg (Equivalent to 15% CV)
z Score
-1.0 -0.5 -0.4 -0.3 -0.2 -0.2 0.1 0.6 0.7 2.3
Laboratory
8 9 7 19 2 11 14 20 5 1

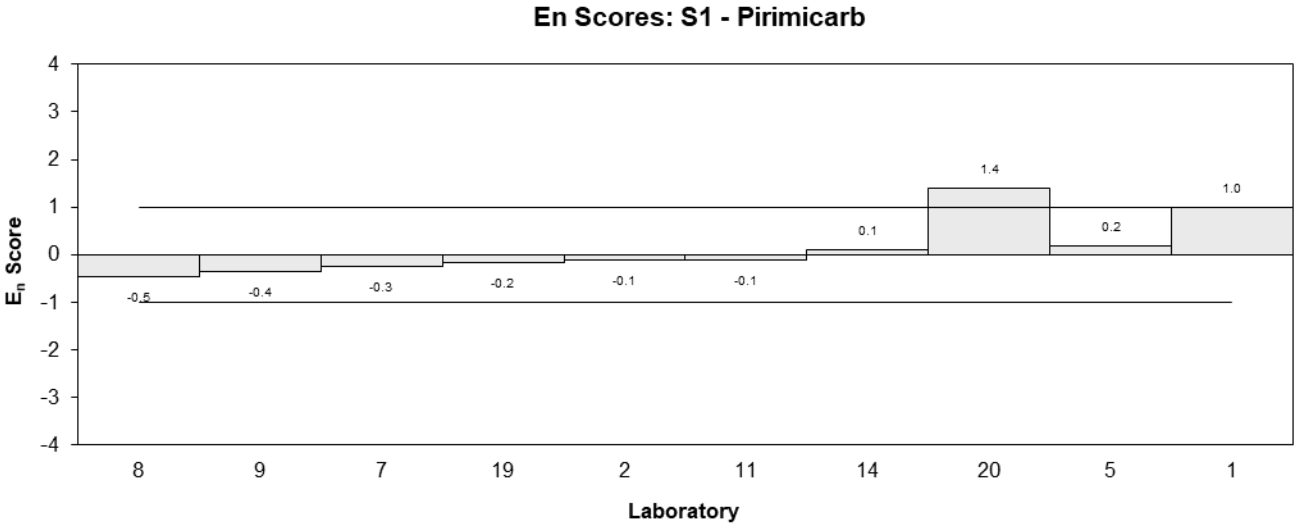

En Scores: S1 - Pirimicarb
En Score
-0.5 -0.4 -0.3 -0.2 -0.1 -0.1 0.1 1.4 0.2 1.0
Laboratory
8 9 7 19 2 11 14 20 5 1

Figure 8

Table 12

**Sample Details**

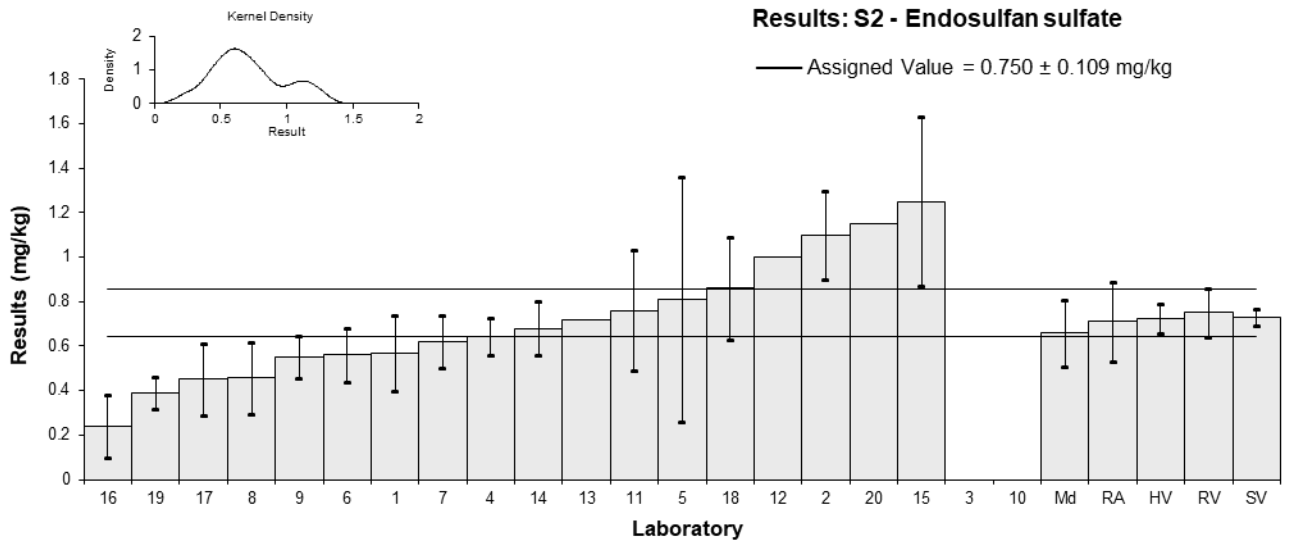
| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Lettuce |
| **Analyte** | Endosulfan sulfate |
| **Unit** | mg/kg |

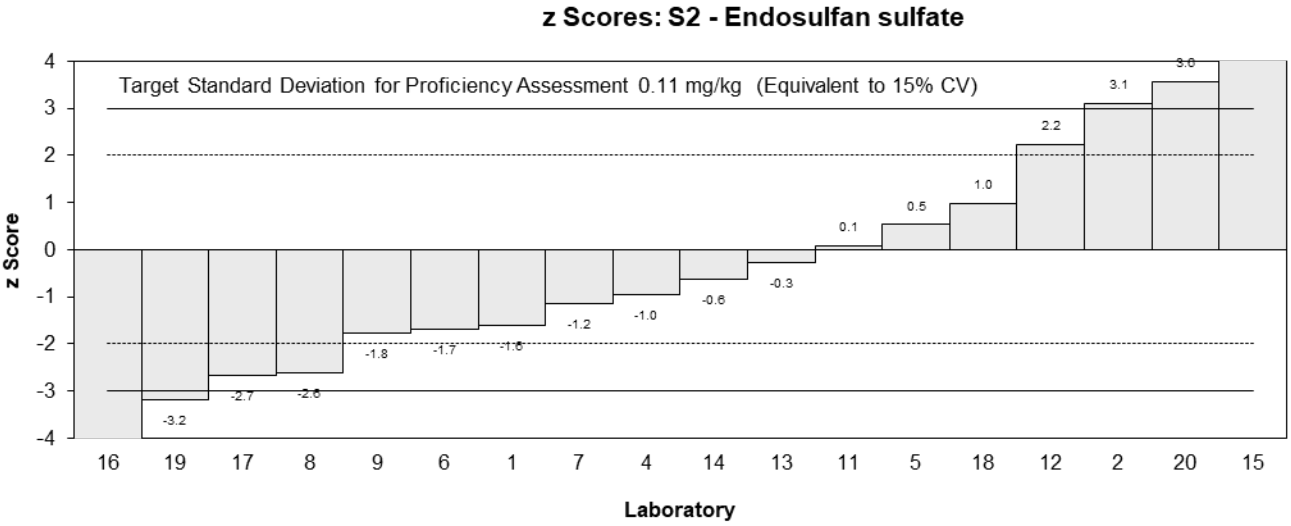
**Participant Results**

| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.57 | 0.17 | 75 | -1.60 | -0.89 |
| **2** | 1.1 | 0.2 | 89 | 3.11 | 1.54 |
| **3** | NR | NR | NR | | |
| **4** | 0.643 | 0.084 | NR | -0.95 | -0.78 |
| **5** | 0.81 | 0.55 | 56 | 0.53 | 0.11 |
| **6** | 0.56 | 0.12 | NR | -1.69 | -1.17 |
| **7** | 0.62 | 0.12 | 96 | -1.16 | -0.80 |
| **8** | 0.456 | 0.160 | 72 | -2.61 | -1.52 |
| **9** | 0.55 | 0.097 | 81 | -1.78 | -1.37 |
| **10** | NT | NT | NT | | |
| **11** | 0.76 | 0.27 | 102 | 0.09 | 0.03 |
| **12** | 1.00 | NR | NR | 2.22 | 2.29 |
| **13** | 0.72 | NR | NR | -0.27 | -0.28 |
| **14** | 0.68 | 0.12 | 95 | -0.62 | -0.43 |
| **15** | 1.25 | 0.38 | 56 | 4.44 | 1.26 |
| **16** | 0.24 | 0.14 | 107 | -4.53 | -2.87 |
| **17** | 0.45 | 0.16 | 69 | -2.67 | -1.55 |
| **18** | 0.86 | 0.23 | 113 | 0.98 | 0.43 |
| **19** | 0.39 | 0.07 | 96.6 | -3.20 | -2.78 |
| **20** | 1.151 | NR | 85 | 3.56 | 3.68 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.750 | 0.109 |
| **Spike Value** | 0.732 | 0.037 |
| **Homogeneity Value** | 0.723 | 0.067 |
| **Reference Value** | 0.750 | 0.109 |
| **Robust Average** | 0.71 | 0.18 |
| **Median** | 0.66 | 0.15 |
| **Mean** | 0.71 | |
| **N** | 18 | |
| **Max** | 1.25 | |
| **Min** | 0.24 | |
| **Robust SD** | 0.30 | |
| **Robust CV** | 42% | |


Kernel Density
Density
Result
Results: S2 - Endosulfan sulfate
Assigned Value = 0.750 ± 0.109 mg/kg
Results (mg/kg)
16 19 17 8 9 6 1 7 4 14 13 11 5 18 12 2 20 15 3 10 Md RA HV RV SV
Laboratory


z Scores: S2 - Endosulfan sulfate
Target Standard Deviation for Proficiency Assessment 0.11 mg/kg (Equivalent to 15% CV)
z Score
16 19 17 8 9 6 1 7 4 14 13 11 5 18 12 2 20 15
Laboratory

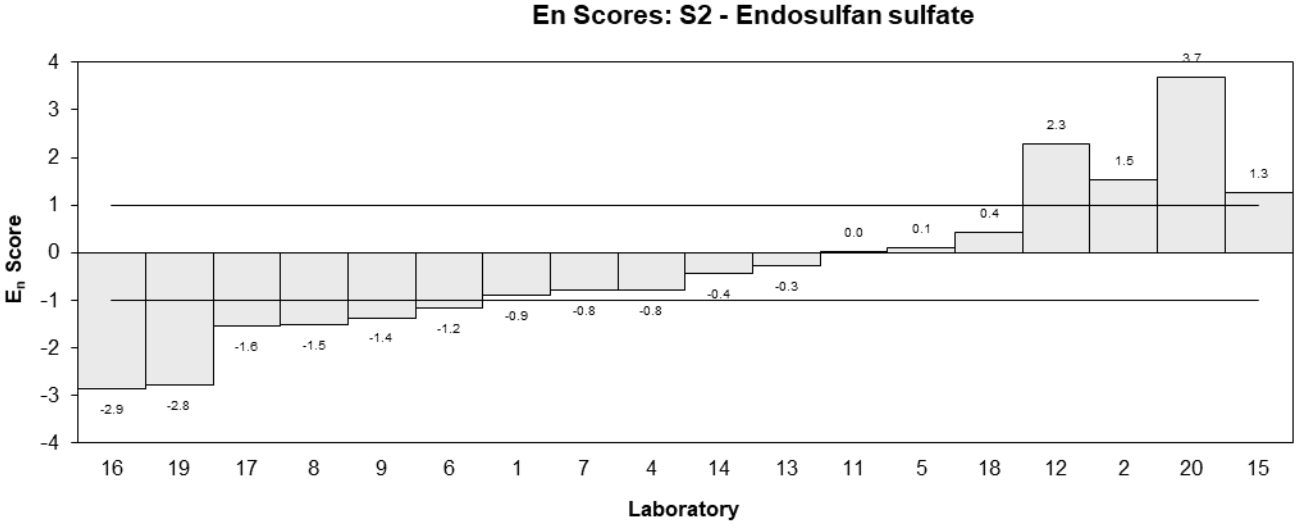

En Scores: S2 - Endosulfan sulfate
En Score
16 19 17 8 9 6 1 7 4 14 13 11 5 18 12 2 20 15
Laboratory

Figure 9

Table 13

**Sample Details**

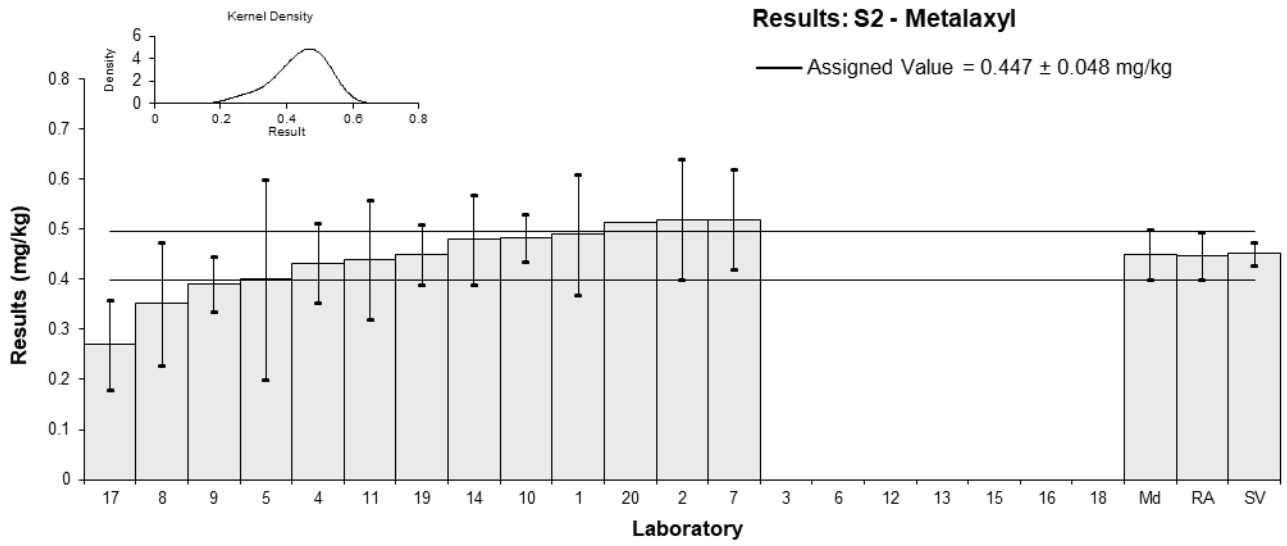
| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Lettuce |
| **Analyte** | Metalaxyl |
| **Unit** | mg/kg |

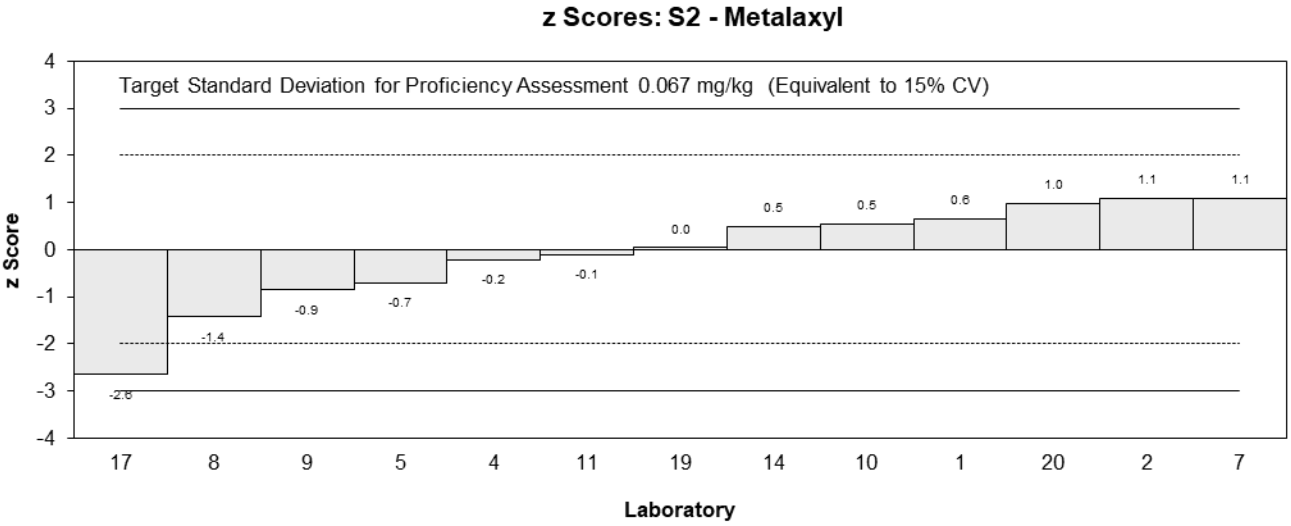
**Participant Results**

| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.49 | 0.12 | 97 | 0.64 | 0.33 |
| **2** | 0.52 | 0.12 | 80 | 1.09 | 0.56 |
| **3** | NT | NT | NT | | |
| **4** | 0.433 | 0.079 | NR | -0.21 | -0.15 |
| **5** | 0.4 | 0.2 | 149 | -0.70 | -0.23 |
| **6** | NT | NT | NT | | |
| **7** | 0.52 | 0.10 | 99 | 1.09 | 0.66 |
| **8** | 0.352 | 0.123 | 85 | -1.42 | -0.72 |
| **9** | 0.39 | 0.055 | 95 | -0.85 | -0.78 |
| **10** | 0.483 | 0.048 | 84 | 0.54 | 0.53 |
| **11** | 0.44 | 0.12 | 88 | -0.10 | -0.05 |
| **12** | NT | NT | NT | | |
| **13** | NR | NR | NR | | |
| **14** | 0.48 | 0.09 | 85 | 0.49 | 0.32 |
| **15** | NT | NT | NT | | |
| **16** | NT | NT | NT | | |
| **17** | 0.27 | 0.09 | 64 | -2.64 | -1.74 |
| **18** | NT | NT | NT | | |
| **19** | 0.45 | 0.06 | 95.3 | 0.04 | 0.04 |
| **20** | 0.513 | NR | 81 | 0.98 | 1.38 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.447 | 0.048 |
| **Spike Value** | 0.452 | 0.023 |
| **Robust Average** | 0.447 | 0.048 |
| **Median** | 0.450 | 0.051 |
| **Mean** | 0.442 | |
| **N** | 13 | |
| **Max** | 0.52 | |
| **Min** | 0.27 | |
| **Robust SD** | 0.069 | |
| **Robust CV** | 15% | |


Kernel Density
Density
Result
Results: S2 - Metalaxyl
Assigned Value = 0.447 ± 0.048 mg/kg
Results (mg/kg)
Laboratory
17 8 9 5 4 11 19 14 10 1 20 2 7 3 6 12 13 15 16 18 Md RA SV


z Scores: S2 - Metalaxyl
Target Standard Deviation for Proficiency Assessment 0.067 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
17 8 9 5 4 11 19 14 10 1 20 2 7
-2.6 -1.4 -0.9 -0.7 -0.2 -0.1 0.0 0.5 0.5 0.6 1.0 1.1 1.1

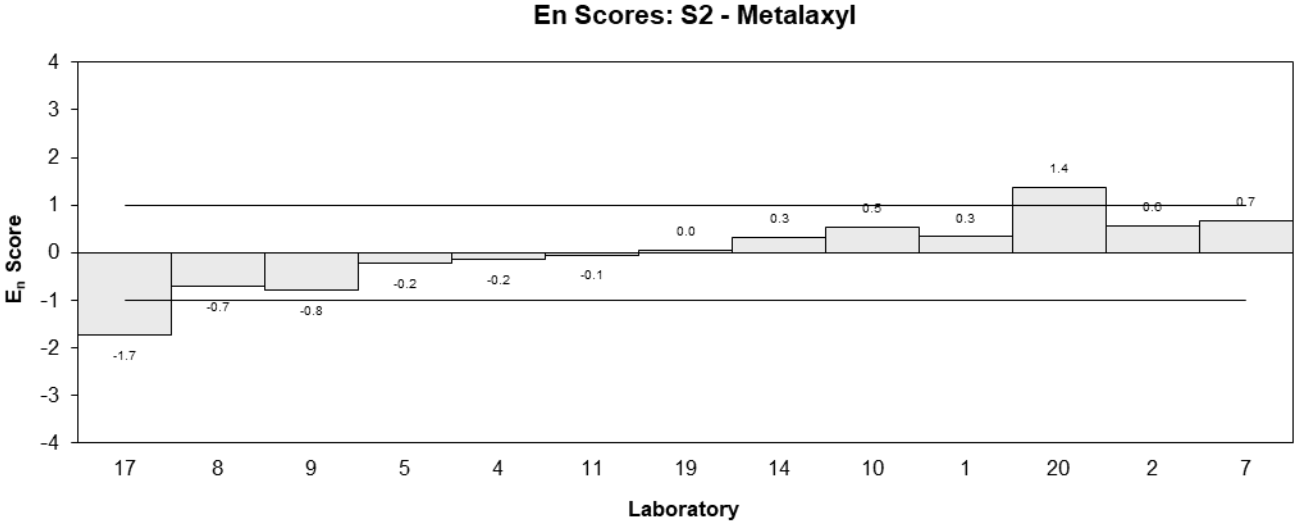

En Scores: S2 - Metalaxyl
En Score
Laboratory
17 8 9 5 4 11 19 14 10 1 20 2 7
-1.7 -0.7 -0.8 -0.2 -0.2 -0.1 0.0 0.3 0.5 0.3 1.4 0.6 0.7

Figure 10

Table 14

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Lettuce |
| **Analyte** | Permethrin |
| **Unit** | mg/kg |

**Participant Results**

| Lab. Code | Result | Uncertainty | Rec |
|---|---|---|---|
| **1** | 0.15 | 0.045 | 65 |
| **2** | 0.21 | 0.05 | 107 |
| **3** | 0.112 | NR | 113.79 |
| **4** | 0.105 | 0.020 | NR |
| **5** | 0.2 | 0.1 | 34 |
| **6** | NT | NT | NT |
| **7** | 0.19 | 0.038 | 111 |
| **8** | 0.105 | 0.037 | 81 |
| **9** | 0.28 | 0.02 | 89 |
| **10** | NT | NT | NT |
| **11** | 0.21 | 0.069 | 97 |
| **12** | 0.30 | NR | NR |
| **13** | NR | NR | NR |
| **14** | 0.15 | 0.03 | 96 |
| **15** | 0.12 | 0.05 | 115 |
| **16** | 0.05 | 0.02 | 115 |
| **17** | 0.03 | 0.01 | 85 |
| **18** | 0.25 | 0.07 | 81 |
| **19** | 0.08 | 0.01 | 87.3 |
| **20** | NR | NR | NR |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | Not Set | |
| **Spike Value** | 0.152 | 0.008 |
| **Robust Average** | 0.158 | 0.056 |
| **Median** | 0.150 | 0.051 |
| **Mean** | 0.159 | |
| **N** | 16 | |
| **Max** | 0.3 | |
| **Min** | 0.03 | |
| **Robust SD** | 0.089 | |
| **Robust CV** | 56% | |

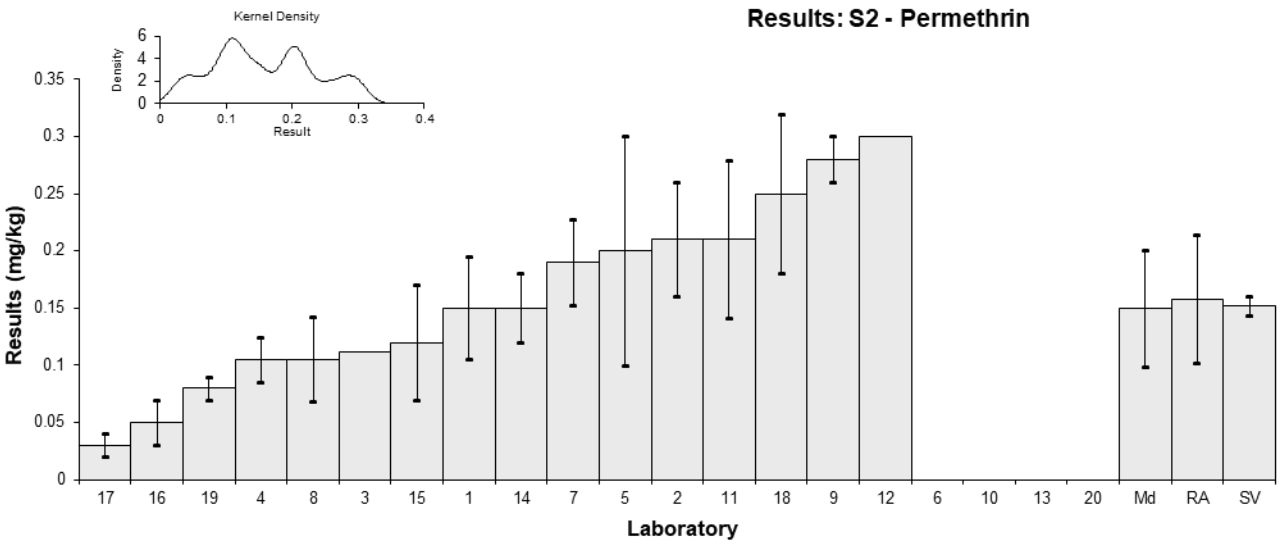

Results: S2 - Permethrin
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
17 16 19 4 8 3 15 1 14 7 5 2 11 18 9 12 6 10 13 20 Md RA SV

Figure 11

Table 15

**Sample Details**

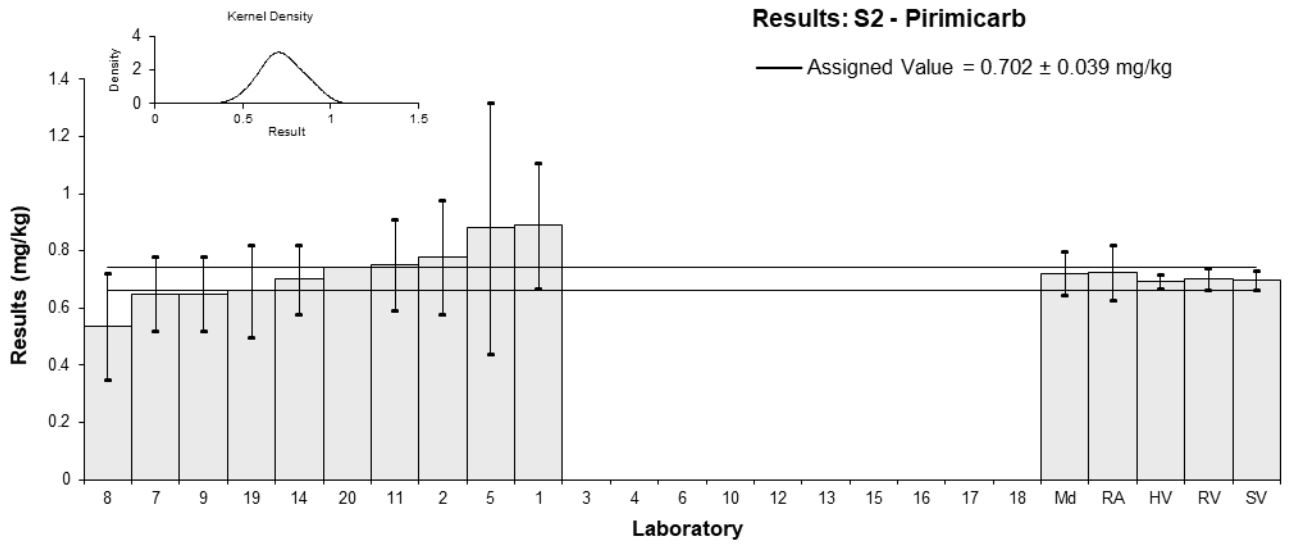
| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Lettuce |
| **Analyte** | Pirimicarb |
| **Unit** | mg/kg |

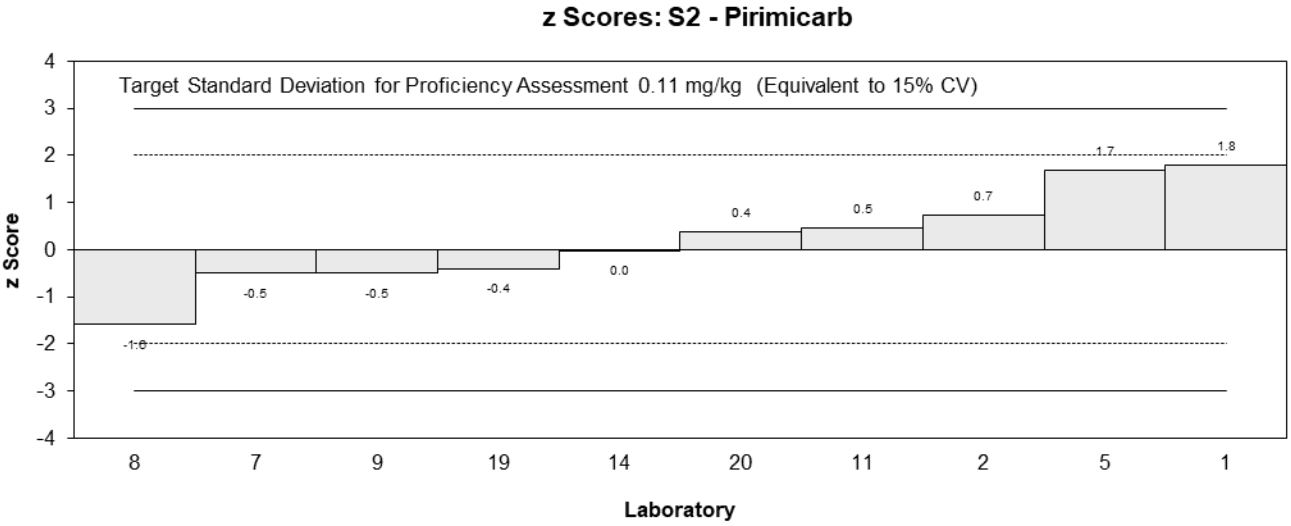
**Participant Results**

| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.89 | 0.22 | 95 | 1.79 | 0.84 |
| **2** | 0.78 | 0.2 | 64 | 0.74 | 0.38 |
| **3** | NT | NT | NT | | |
| **4** | NT | NT | NT | | |
| **5** | 0.88 | 0.44 | 132 | 1.69 | 0.40 |
| **6** | NT | NT | NT | | |
| **7** | 0.65 | 0.13 | 105 | -0.49 | -0.38 |
| **8** | 0.535 | 0.187 | 93 | -1.59 | -0.87 |
| **9** | 0.65 | 0.13 | 86 | -0.49 | -0.38 |
| **10** | NT | NT | NT | | |
| **11** | 0.75 | 0.16 | 95 | 0.46 | 0.29 |
| **12** | NT | NT | NT | | |
| **13** | NR | NR | NR | | |
| **14** | 0.70 | 0.12 | 91 | -0.02 | -0.02 |
| **15** | NT | NT | NT | | |
| **16** | NT | NT | NT | | |
| **17** | NT | NT | NT | | |
| **18** | NT | NT | NT | | |
| **19** | 0.66 | 0.16 | 93.1 | -0.40 | -0.26 |
| **20** | 0.743 | NR | 94 | 0.39 | 1.05 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.702 | 0.039 |
| **Spike Value** | 0.697 | 0.035 |
| **Homogeneity Value** | 0.693 | 0.024 |
| **Reference Value** | 0.702 | 0.039 |
| **Robust Average** | 0.724 | 0.097 |
| **Median** | 0.722 | 0.078 |
| **Mean** | 0.724 | |
| **N** | 10 | |
| **Max** | 0.89 | |
| **Min** | 0.535 | |
| **Robust SD** | 0.12 | |
| **Robust CV** | 17% | |


Kernel Density
Density
Result
Results: S2 - Pirimicarb
Assigned Value = 0.702 ± 0.039 mg/kg
Results (mg/kg)
Laboratory
8 7 9 19 14 20 11 2 5 1 3 4 6 10 12 13 15 16 17 18 Md RA HV RV SV


z Scores: S2 - Pirimicarb
Target Standard Deviation for Proficiency Assessment 0.11 mg/kg (Equivalent to 15% CV)
z Score
-1.6 -0.5 -0.5 -0.4 0.0 0.4 0.5 0.7 1.7 1.8
Laboratory
8 7 9 19 14 20 11 2 5 1

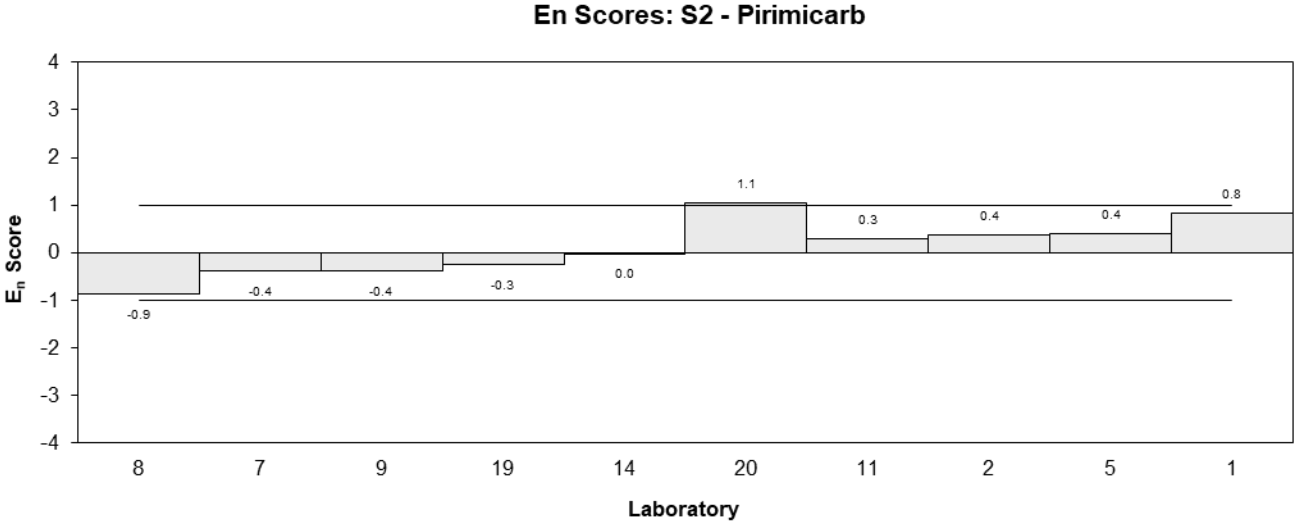

En Scores: S2 - Pirimicarb
En Score
-0.9 -0.4 -0.4 -0.3 0.0 1.1 0.3 0.4 0.4 0.8
Laboratory
8 7 9 19 14 20 11 2 5 1

Figure 12

Table 16

**Sample Details**

| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | Parsley |
| **Analyte** | Chlorpyrifos |
| **Unit** | mg/kg |

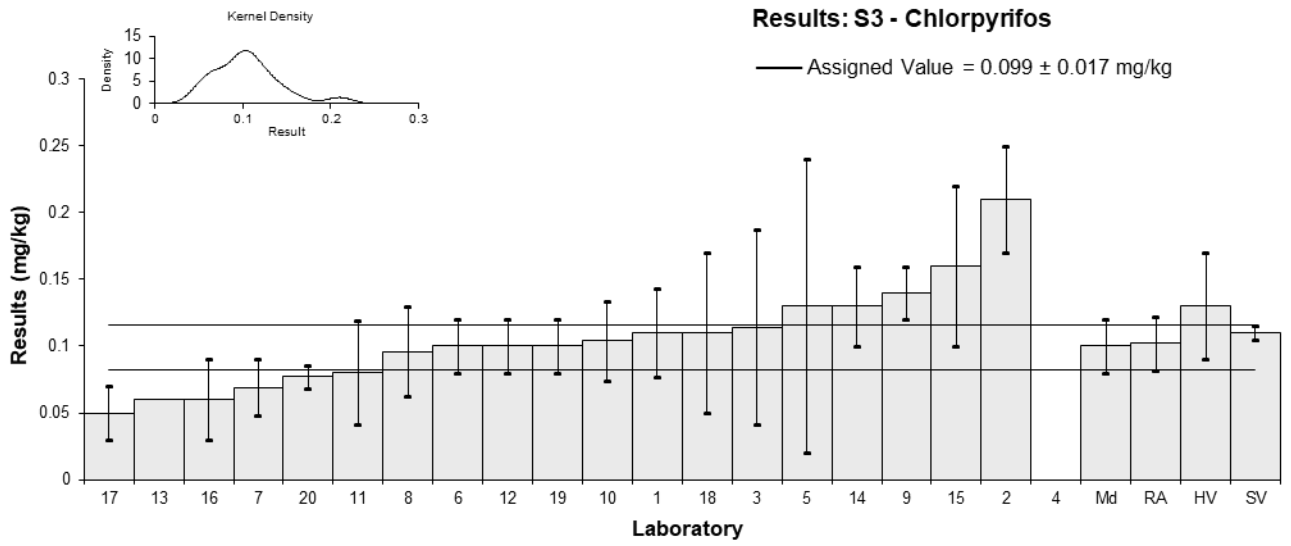
**Participant Results**

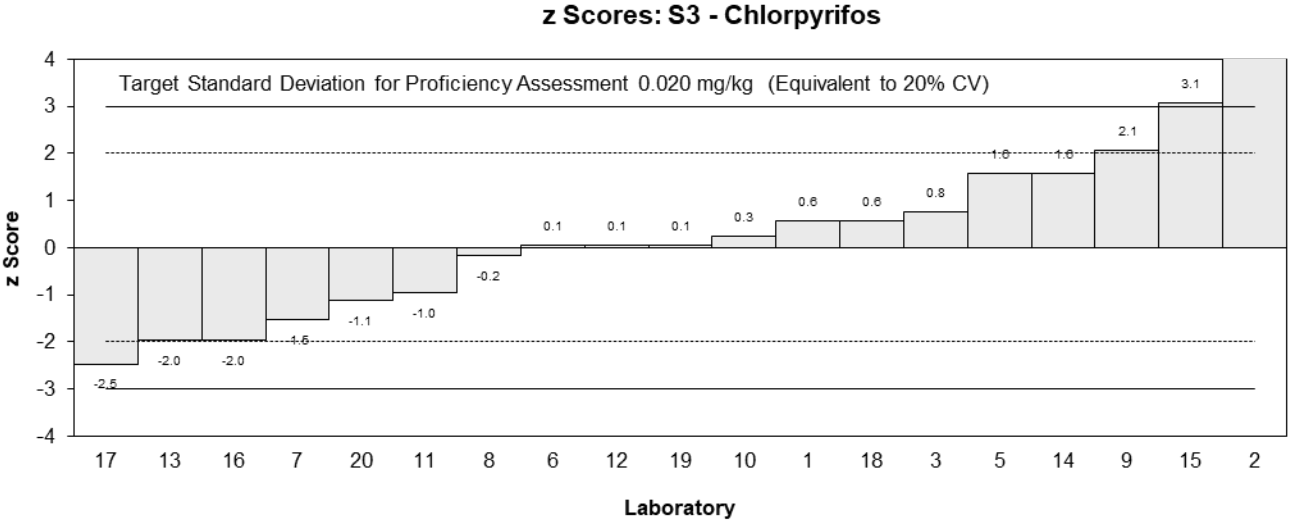
| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.11 | 0.033 | 79 | 0.56 | 0.30 |
| **2*** | 0.21 | 0.04 | 149 | 5.61 | 2.55 |
| **3** | 0.114 | 0.073 | 85.67 | 0.76 | 0.20 |
| **4** | NR | NR | NR | | |
| **5** | 0.13 | 0.11 | 93 | 1.57 | 0.28 |
| **6** | 0.10 | 0.02 | NR | 0.05 | 0.04 |
| **7** | 0.069 | 0.021 | 85 | -1.52 | -1.11 |
| **8** | 0.0959 | 0.0336 | 78 | -0.16 | -0.08 |
| **9** | 0.14 | 0.02 | 102 | 2.07 | 1.56 |
| **10** | 0.104 | 0.03 | 107 | 0.25 | 0.15 |
| **11** | 0.08 | 0.039 | 80 | -0.96 | -0.45 |
| **12** | 0.10 | 0.02 | 78 | 0.05 | 0.04 |
| **13** | 0.06 | NR | NR | -1.97 | -2.29 |
| **14** | 0.13 | 0.03 | 88 | 1.57 | 0.90 |
| **15*** | 0.16 | 0.06 | 99 | 3.08 | 0.98 |
| **16** | 0.06 | 0.03 | 78 | -1.97 | -1.13 |
| **17*** | 0.05 | 0.02 | 110 | -2.47 | -1.87 |
| **18** | 0.11 | 0.06 | 31 | 0.56 | 0.18 |
| **19** | 0.1 | 0.02 | 97.3 | 0.05 | 0.04 |
| **20** | 0.077 | 0.009 | 86 | -1.11 | -1.14 |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.099 | 0.017 |
| **Spike Value** | 0.110 | 0.005 |
| **Homogeneity Value** | 0.13 | 0.04 |
| **Robust Average** | 0.102 | 0.020 |
| **Median** | 0.100 | 0.020 |
| **Mean** | 0.105 | |
| **N** | 19 | |
| **Max** | 0.21 | |
| **Min** | 0.05 | |
| **Robust SD** | 0.035 | |
| **Robust CV** | 34% | |


Kernel Density
Density
Result
Results: S3 - Chlorpyrifos
Assigned Value = 0.099 ± 0.017 mg/kg
Results (mg/kg)
Laboratory
17 13 16 7 20 11 8 6 12 19 10 1 18 3 5 14 9 15 2 4 Md RA HV SV


z Scores: S3 - Chlorpyrifos
Target Standard Deviation for Proficiency Assessment 0.020 mg/kg (Equivalent to 20% CV)
z Score
Laboratory
17 13 16 7 20 11 8 6 12 19 10 1 18 3 5 14 9 15 2

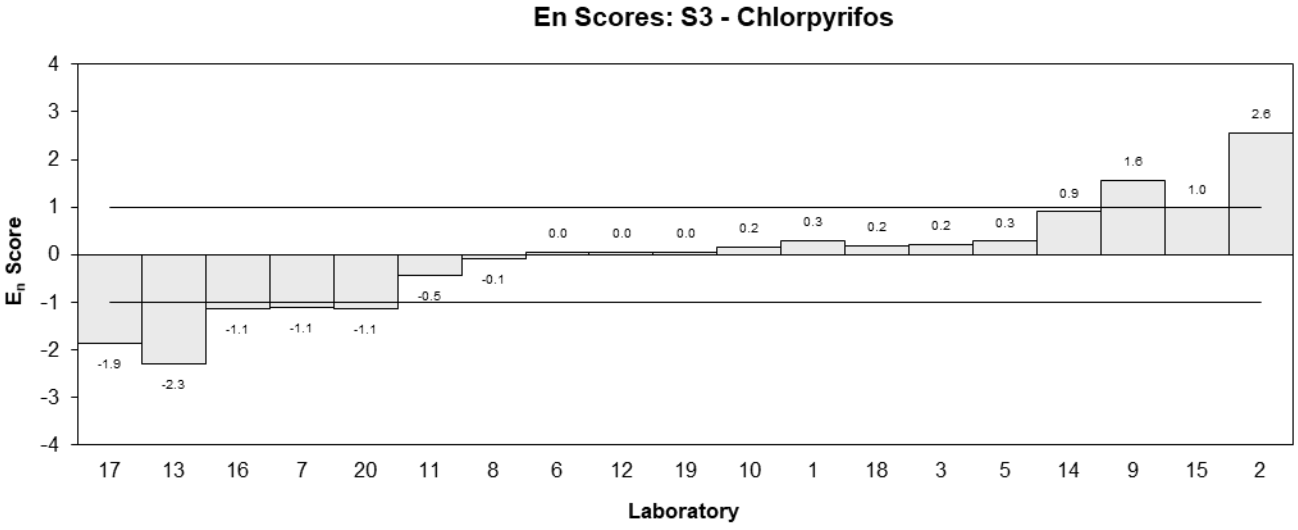

En Scores: S3 - Chlorpyrifos
En Score
Laboratory
17 13 16 7 20 11 8 6 12 19 10 1 18 3 5 14 9 15 2

Figure 13

Table 17

**Sample Details**

| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | Parsley |
| **Analyte** | Imidacloprid |
| **Unit** | mg/kg |

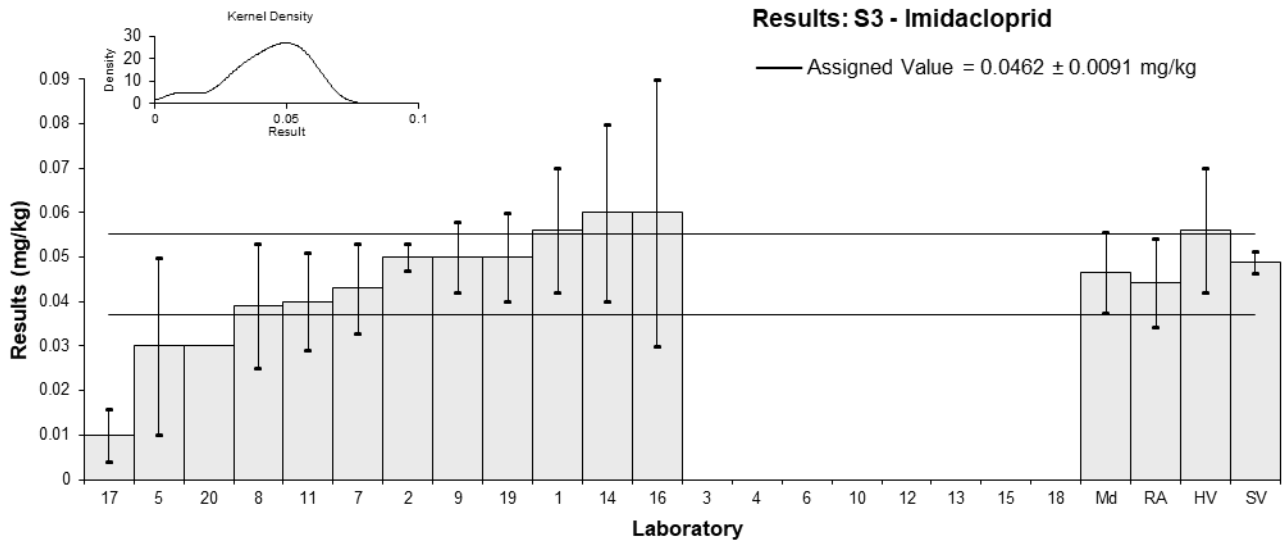
**Participant Results**

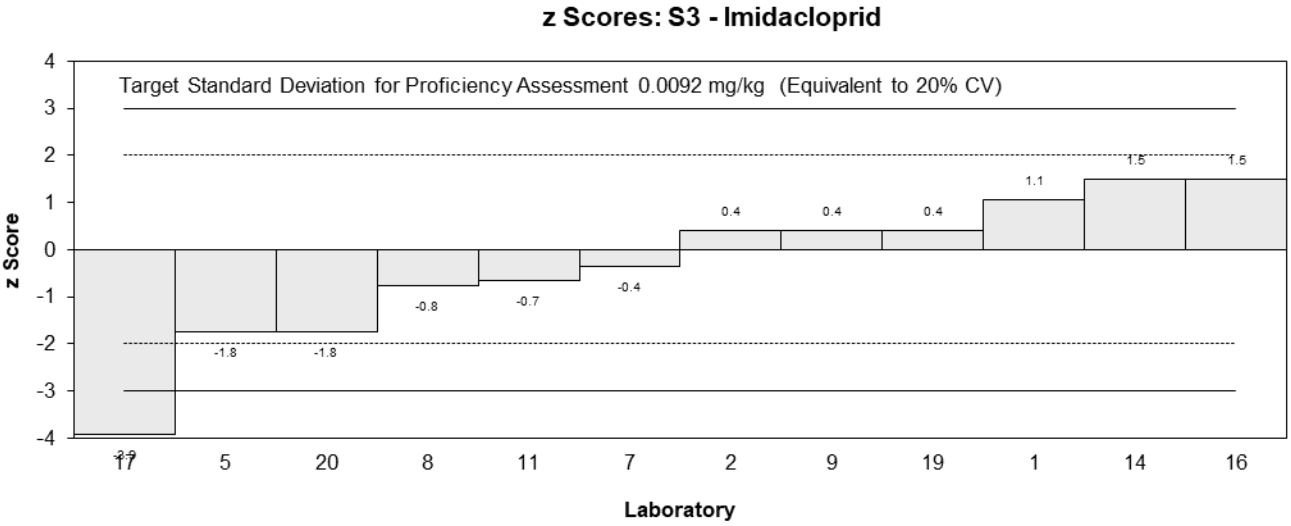
| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.056 | 0.014 | 105 | 1.06 | 0.59 |
| **2** | 0.05 | 0.003 | 88 | 0.41 | 0.40 |
| **3** | NT | NT | NT | | |
| **4** | NT | NT | NT | | |
| **5** | 0.03 | 0.02 | 51 | -1.75 | -0.74 |
| **6** | NT | NT | NT | | |
| **7** | 0.043 | 0.010 | 101 | -0.35 | -0.24 |
| **8** | 0.039 | 0.014 | 73 | -0.78 | -0.43 |
| **9** | 0.05 | 0.008 | 80 | 0.41 | 0.31 |
| **10** | NT | NT | NT | | |
| **11** | 0.04 | 0.011 | 73 | -0.67 | -0.43 |
| **12** | NT | NT | NT | | |
| **13** | NR | NR | NR | | |
| **14** | 0.06 | 0.02 | 94 | 1.49 | 0.63 |
| **15** | NT | NT | NT | | |
| **16** | 0.06 | 0.03 | 129 | 1.49 | 0.44 |
| **17*** | 0.01 | 0.006 | 46 | -3.92 | -3.32 |
| **18** | NT | NT | NT | | |
| **19** | 0.05 | 0.01 | 95.8 | 0.41 | 0.28 |
| **20** | 0.03 | NR | 90 | -1.75 | -1.78 |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.0462 | 0.0091 |
| **Spike Value** | 0.0489 | 0.0024 |
| **Homogeneity Value** | 0.056 | 0.014 |
| **Robust Average** | 0.0443 | 0.0099 |
| **Median** | 0.0465 | 0.0091 |
| **Mean** | 0.0432 | |
| **N** | 12 | |
| **Max** | 0.06 | |
| **Min** | 0.01 | |
| **Robust SD** | 0.014 | |
| **Robust CV** | 31% | |


Kernel Density
Density
Result
Results: S3 - Imidacloprid
Assigned Value = 0.0462 ± 0.0091 mg/kg
Results (mg/kg)
Laboratory
17 5 20 8 11 7 2 9 19 1 14 16 3 4 6 10 12 13 15 18 Md RA HV SV


z Scores: S3 - Imidacloprid
Target Standard Deviation for Proficiency Assessment 0.0092 mg/kg (Equivalent to 20% CV)
z Score
Laboratory
17 5 20 8 11 7 2 9 19 1 14 16

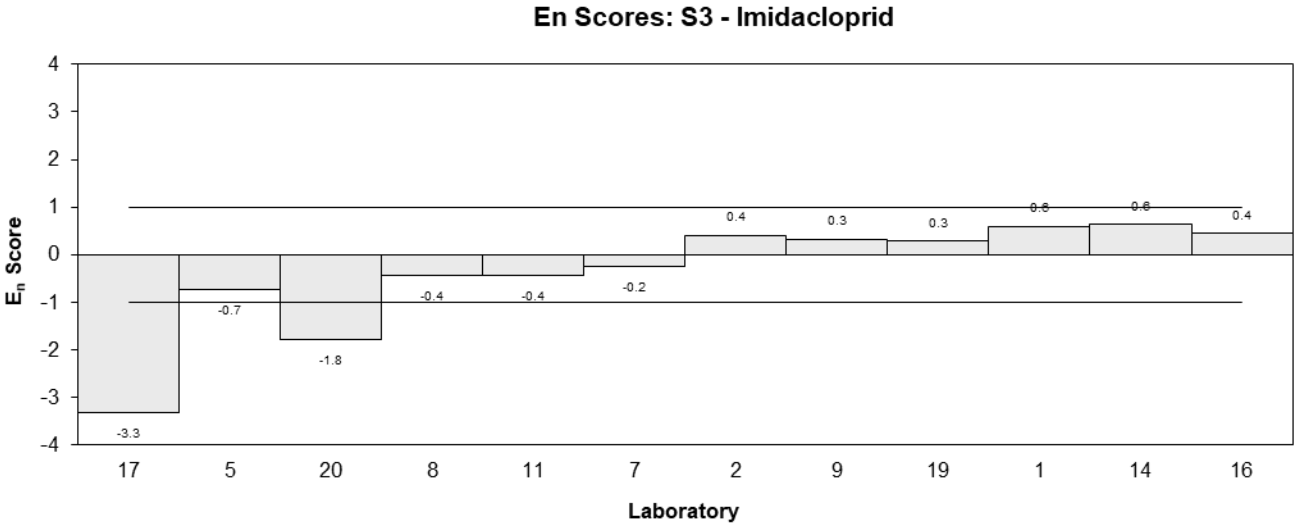

En Scores: S3 - Imidacloprid
En Score
Laboratory
17 5 20 8 11 7 2 9 19 1 14 16

Figure 14

Table 18

**Sample Details**

| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | Parsley |
| **Analyte** | Linuron |
| **Unit** | mg/kg |

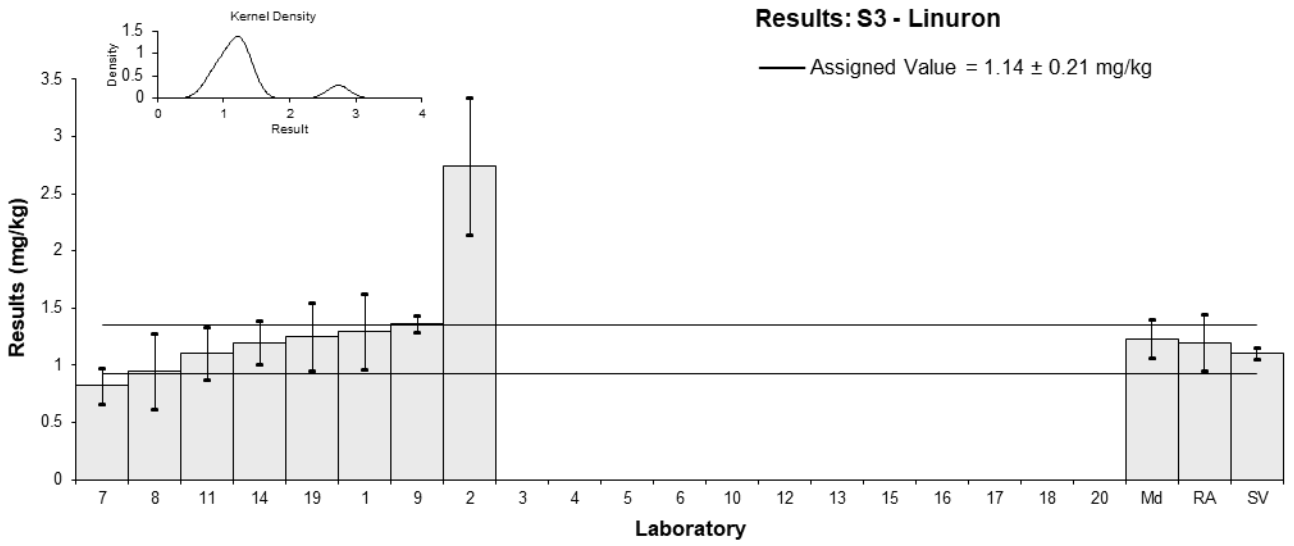
**Participant Results**

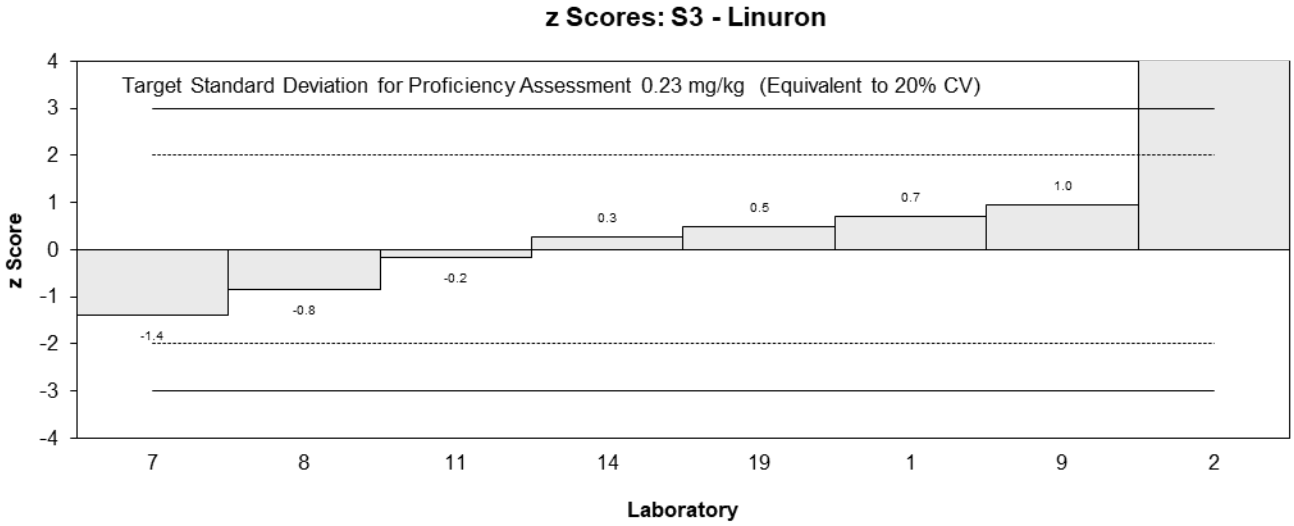
| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 1.3 | 0.33 | 112 | 0.70 | 0.41 |
| **2*** | 2.74 | 0.6 | 89 | 7.02 | 2.52 |
| **3** | NT | NT | NT | | |
| **4** | NT | NT | NT | | |
| **5** | NT | NT | NT | | |
| **6** | NT | NT | NT | | |
| **7** | 0.82 | 0.16 | 95 | -1.40 | -1.21 |
| **8** | 0.948 | 0.332 | 77 | -0.84 | -0.49 |
| **9** | 1.36 | 0.072 | 108 | 0.96 | 0.99 |
| **10** | NT | NT | NT | | |
| **11** | 1.1 | 0.23 | 93 | -0.18 | -0.13 |
| **12** | NT | NT | NT | | |
| **13** | NR | NR | NR | | |
| **14** | 1.2 | 0.19 | 77 | 0.26 | 0.21 |
| **15** | NT | NT | NT | | |
| **16** | NT | NT | NT | | |
| **17** | NT | NT | NT | | |
| **18** | NT | NT | NT | | |
| **19** | 1.25 | 0.3 | 81.2 | 0.48 | 0.30 |
| **20** | NT | NT | NT | | |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1.14 | 0.21 |
| **Spike Value** | 1.10 | 0.05 |
| **Robust Average** | 1.20 | 0.25 |
| **Median** | 1.23 | 0.17 |
| **Mean** | 1.34 | |
| **N** | 8 | |
| **Max** | 2.74 | |
| **Min** | 0.82 | |
| **Robust SD** | 0.28 | |
| **Robust CV** | 24% | |


Kernel Density
Density
Result
Results: S3 - Linuron
Assigned Value = 1.14 ± 0.21 mg/kg
Results (mg/kg)
Laboratory
7 8 11 14 19 1 9 2 3 4 5 6 10 12 13 15 16 17 18 20 Md RA SV


z Scores: S3 - Linuron
Target Standard Deviation for Proficiency Assessment 0.23 mg/kg (Equivalent to 20% CV)
z Score
-1.4
-0.8
-0.2
0.3
0.5
0.7
1.0
Laboratory
7 8 11 14 19 1 9 2

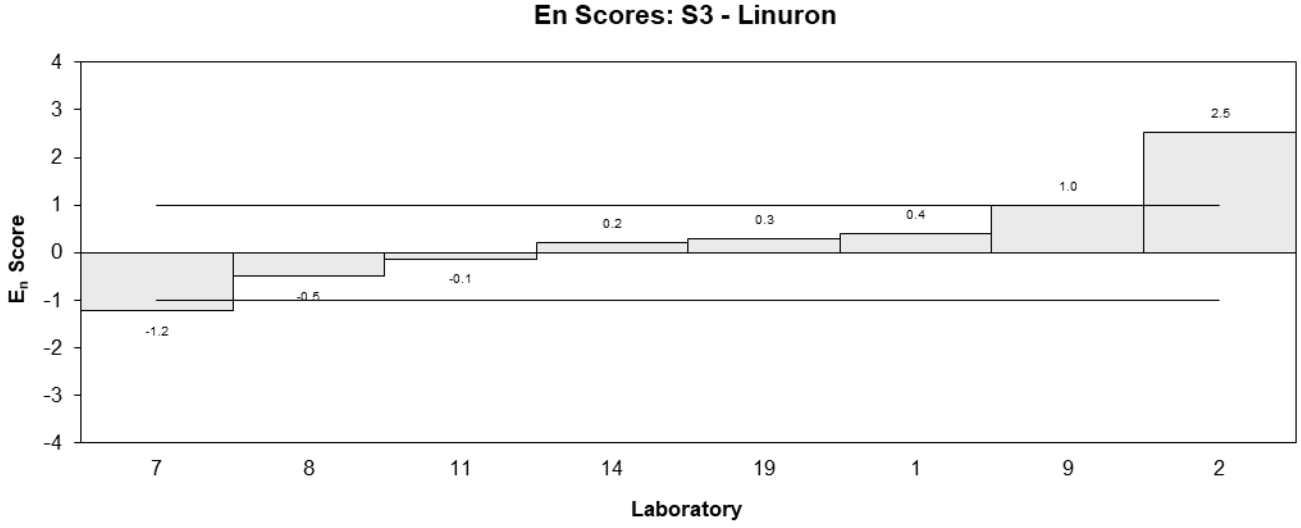

En Scores: S3 - Linuron
En Score
-1.2
-0.5
-0.1
0.2
0.3
0.4
1.0
2.5
Laboratory
7 8 11 14 19 1 9 2

Figure 15

Table 19

**Sample Details**

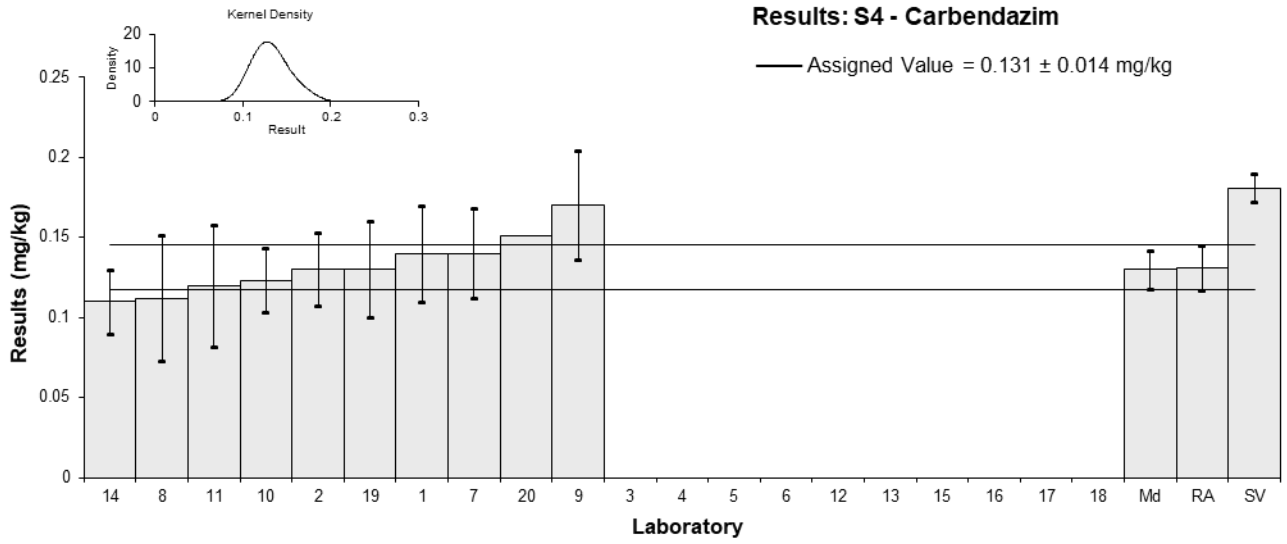
| | |
|---|---|
| **Sample No.** | S4 |
| **Matrix** | Green Bean |
| **Analyte** | Carbendazim |
| **Unit** | mg/kg |

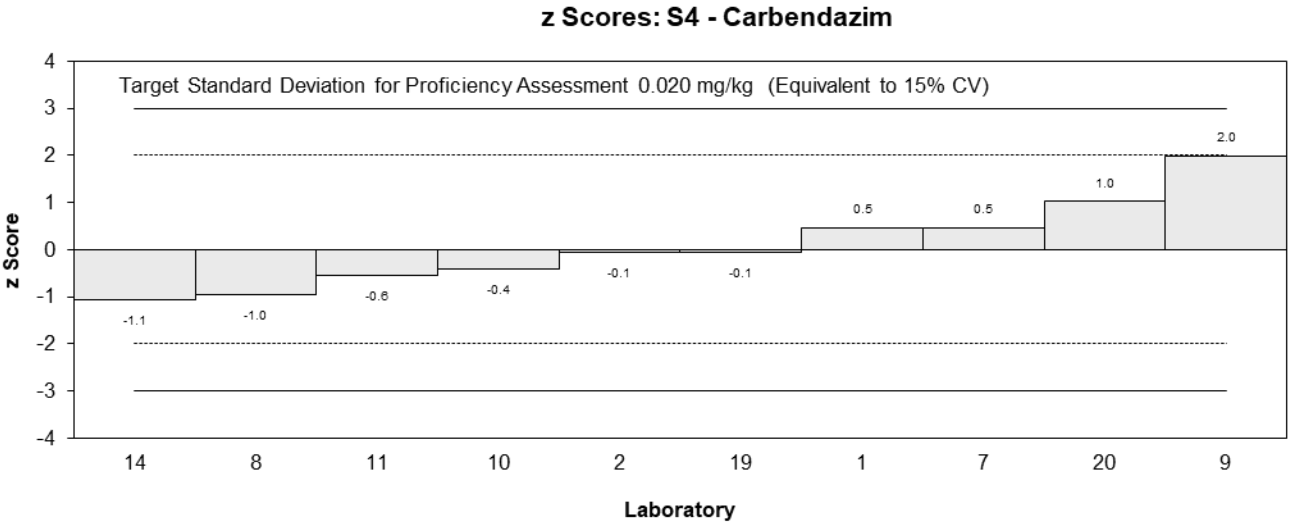
**Participant Results**

| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 0.14 | 0.03 | 94 | 0.46 | 0.27 |
| **2** | 0.13 | 0.023 | 62 | -0.05 | -0.04 |
| **3** | NT | NT | NT | | |
| **4** | NT | NT | NT | | |
| **5** | NT | NT | NT | | |
| **6** | NT | NT | NT | | |
| **7** | 0.14 | 0.028 | 96 | 0.46 | 0.29 |
| **8** | 0.112 | 0.039 | 74 | -0.97 | -0.46 |
| **9** | 0.17 | 0.034 | 75 | 1.98 | 1.06 |
| **10** | 0.123 | 0.02 | 93 | -0.41 | -0.33 |
| **11** | 0.12 | 0.038 | 84 | -0.56 | -0.27 |
| **12** | NT | NT | NT | | |
| **13** | NR | NR | NR | | |
| **14** | 0.11 | 0.02 | 100 | -1.07 | -0.86 |
| **15** | NT | NT | NT | | |
| **16** | NR | NR | NR | | |
| **17** | NT | NT | NT | | |
| **18** | NT | NT | NT | | |
| **19** | 0.13 | 0.03 | 93.4 | -0.05 | -0.03 |
| **20** | 0.151 | NR | 108 | 1.02 | 1.43 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.131 | 0.014 |
| **Spike Value** | 0.181 | 0.009 |
| **Robust Average** | 0.131 | 0.014 |
| **Median** | 0.130 | 0.012 |
| **Mean** | 0.133 | |
| **N** | 10 | |
| **Max** | 0.17 | |
| **Min** | 0.11 | |
| **Robust SD** | 0.018 | |
| **Robust CV** | 14% | |


Kernel Density
Density
Result
Results: S4 - Carbendazim
Assigned Value = 0.131 ± 0.014 mg/kg
Results (mg/kg)
Laboratory
14 8 11 10 2 19 1 7 20 9 3 4 5 6 12 13 15 16 17 18 Md RA SV


z Scores: S4 - Carbendazim
Target Standard Deviation for Proficiency Assessment 0.020 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
14 8 11 10 2 19 1 7 20 9
-1.1 -1.0 -0.6 -0.4 -0.1 -0.1 0.5 0.5 1.0 2.0

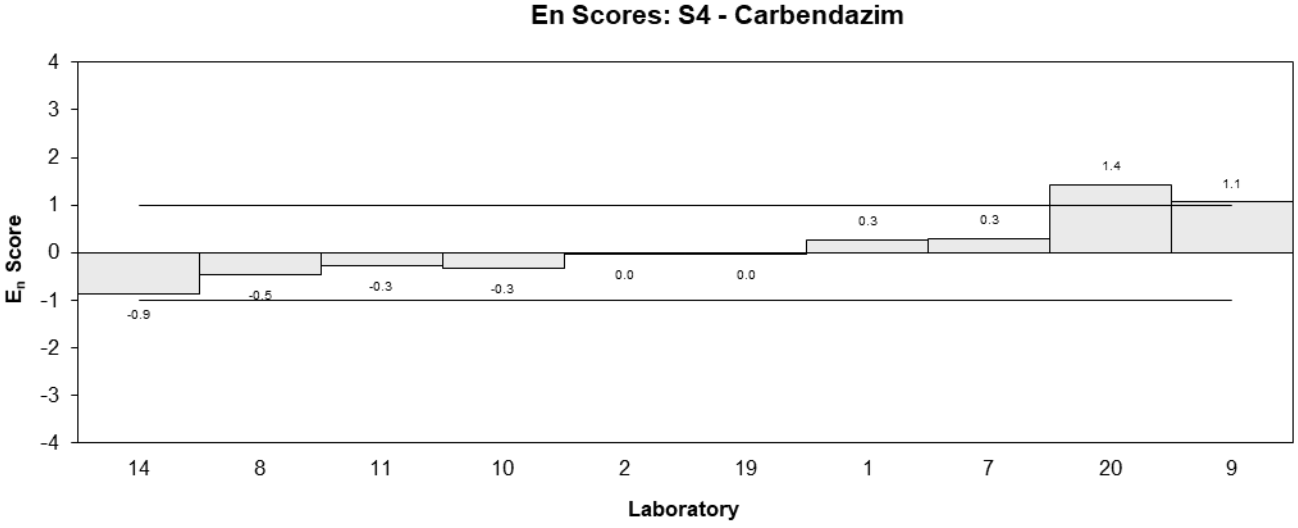

En Scores: S4 - Carbendazim
En Score
Laboratory
14 8 11 10 2 19 1 7 20 9
-0.9 -0.5 -0.3 -0.3 0.0 0.0 0.3 0.3 1.4 1.1

Figure 16

Table 20

**Sample Details**

| | |
|---|---|
| **Sample No.** | S4 |
| **Matrix** | Green Bean |
| **Analyte** | Omethoate |
| **Unit** | mg/kg |

**Participant Results**

| Lab. Code | Result | Uncertainty | Rec |
|---|---|---|---|
| **1** | 2.0 | 0.6 | 86 |
| **2** | 1.15 | 0.31 | 92 |
| **3** | 1.395 | 0.147 | 81.65 |
| **4** | NT | NT | NT |
| **5** | 0.4 | 0.2 | 38 |
| **6** | 1.1 | 0.22 | NR |
| **7** | 2.1 | 0.42 | 93 |
| **8** | 1.508 | 0.528 | 73 |
| **9** | 1.86 | 0.37 | 88 |
| **10** | NT | NT | NT |
| **11** | 2.0 | 0.46 | 86 |
| **12** | 0.98 | 0.18 | 81 |
| **13** | 0.98 | NR | NR |
| **14** | 1.7 | 0.25 | 95 |
| **15** | NT | NT | NT |
| **16** | NT | NT | NT |
| **17** | NT | NT | NT |
| **18** | NT | NT | NT |
| **19** | 1.34 | 0.17 | 80.9 |
| **20** | 1.313 | NR | 76 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | Not Set | |
| **Spike Value** | 1.91 | 0.10 |
| **Robust Average** | 1.44 | 0.33 |
| **Median** | 1.37 | 0.36 |
| **Mean** | 1.42 | |
| **N** | 14 | |
| **Max** | 2.1 | |
| **Min** | 0.4 | |
| **Robust SD** | 0.50 | |
| **Robust CV** | 35% | |

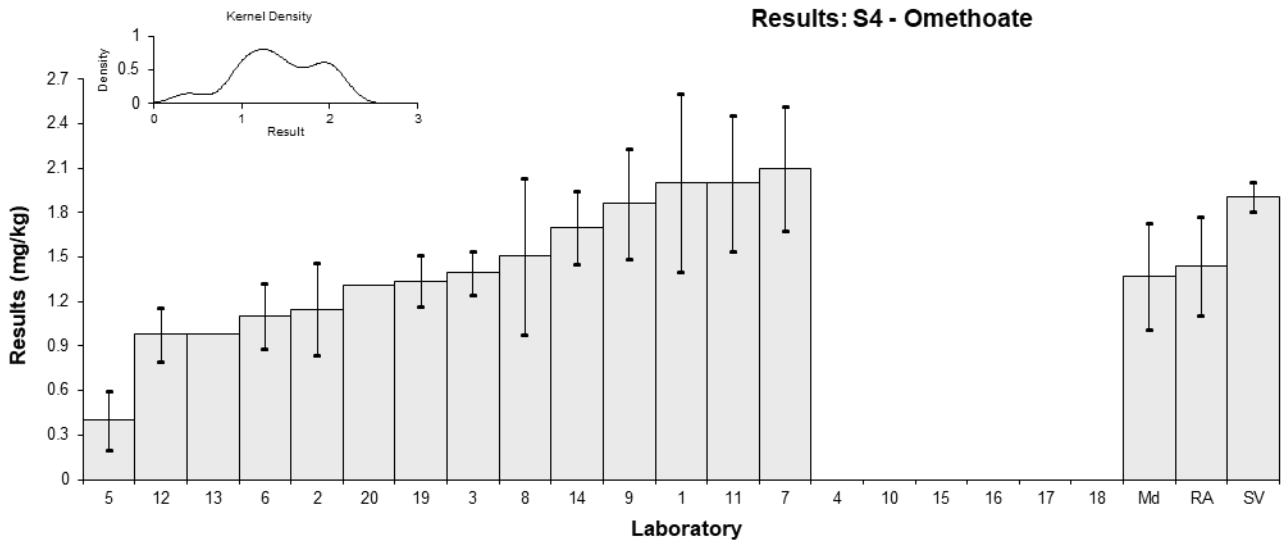

Results: S4 - Omethoate
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
5
12
13
6
2
20
19
3
8
14
9
1
11
7
4
10
15
16
17
18
Md
RA
SV

Figure 17

Table 21

**Sample Details**

| | |
|---|---|
| **Sample No.** | S4 |
| **Matrix** | Green Bean |
| **Analyte** | Pyraclostrobin |
| **Unit** | mg/kg |

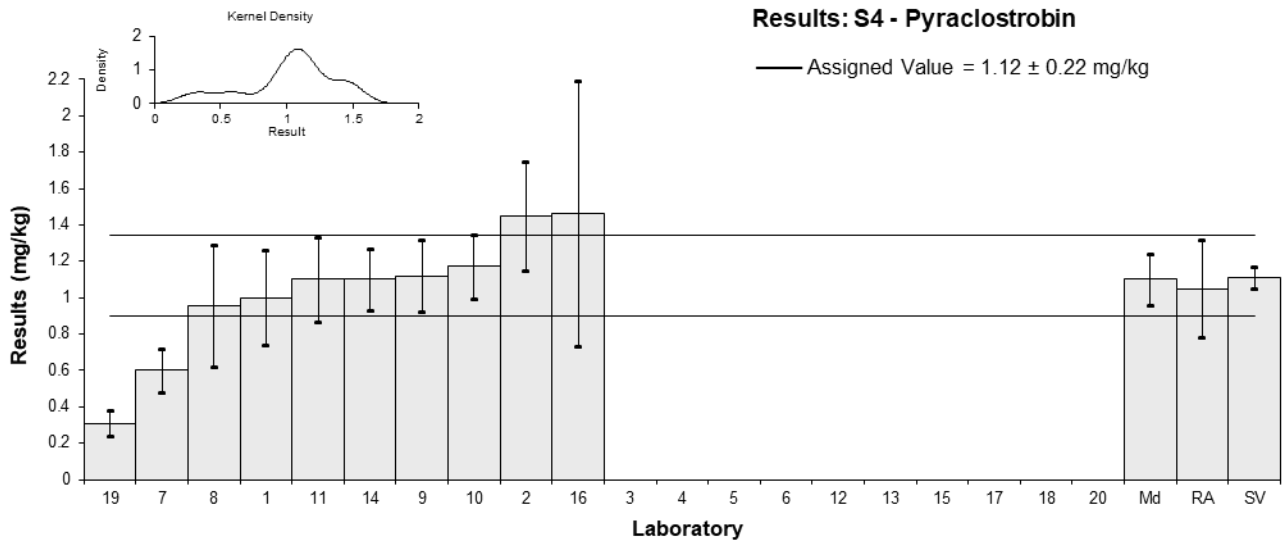
**Participant Results**

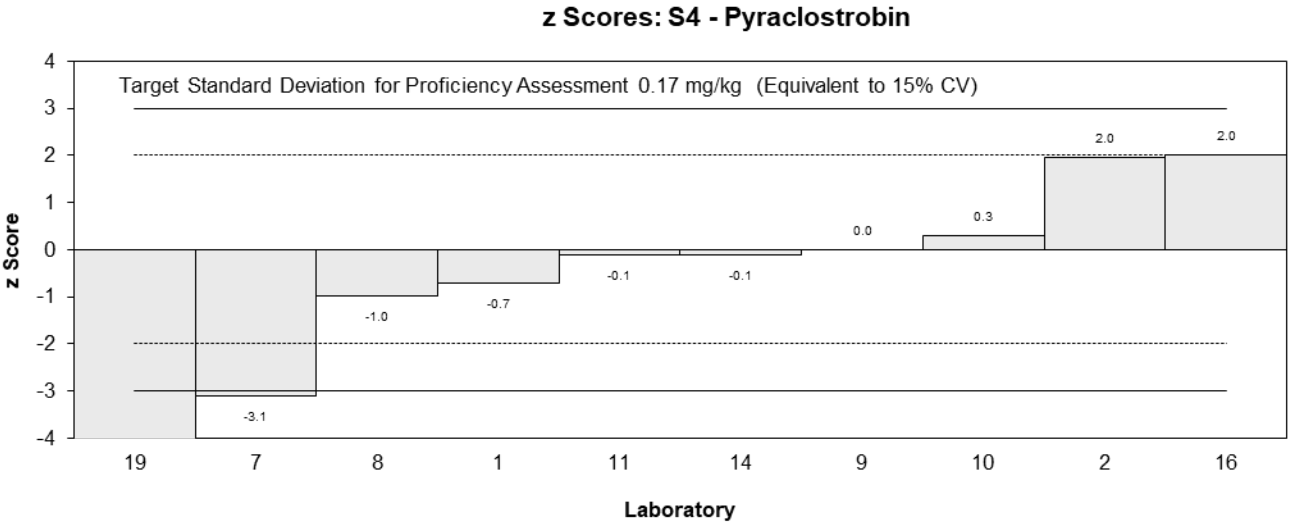
| Lab. Code | Result | Uncertainty | Rec | z | $E_n$ |
|---|---|---|---|---|---|
| **1** | 1.0 | 0.26 | 96 | -0.71 | -0.35 |
| **2** | 1.45 | 0.3 | 96 | 1.96 | 0.89 |
| **3** | NT | NT | NT | | |
| **4** | NT | NT | NT | | |
| **5** | NT | NT | NT | | |
| **6** | NT | NT | NT | | |
| **7** | 0.60 | 0.12 | 100 | -3.10 | -2.08 |
| **8** | 0.954 | 0.334 | 95 | -0.99 | -0.42 |
| **9** | 1.12 | 0.20 | 85 | 0.00 | 0.00 |
| **10** | 1.171 | 0.176 | 116 | 0.30 | 0.18 |
| **11** | 1.1 | 0.23 | 98 | -0.12 | -0.06 |
| **12** | NT | NT | NT | | |
| **13** | NR | NR | NR | | |
| **14** | 1.1 | 0.17 | 88 | -0.12 | -0.07 |
| **15** | NT | NT | NT | | |
| **16** | 1.46 | 0.73 | 127 | 2.02 | 0.45 |
| **17** | NT | NT | NT | | |
| **18** | NT | NT | NT | | |
| **19*** | 0.31 | 0.07 | 92.1 | -4.82 | -3.51 |
| **20** | NT | NT | NT | | |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1.12 | 0.22 |
| **Spike Value** | 1.11 | 0.06 |
| **Robust Average** | 1.05 | 0.27 |
| **Median** | 1.10 | 0.14 |
| **Mean** | 1.03 | |
| **N** | 10 | |
| **Max** | 1.46 | |
| **Min** | 0.31 | |
| **Robust SD** | 0.35 | |
| **Robust CV** | 33% | |


Kernel Density
Density
Result
Results: S4 - Pyraclostrobin
Assigned Value = 1.12 ± 0.22 mg/kg
Results (mg/kg)
Laboratory
19 7 8 1 11 14 9 10 2 16 3 4 5 6 12 13 15 17 18 20 Md RA SV


z Scores: S4 - Pyraclostrobin
Target Standard Deviation for Proficiency Assessment 0.17 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
19 7 8 1 11 14 9 10 2 16
-3.1
-1.0
-0.7
-0.1
-0.1
0.0
0.3
2.0
2.0

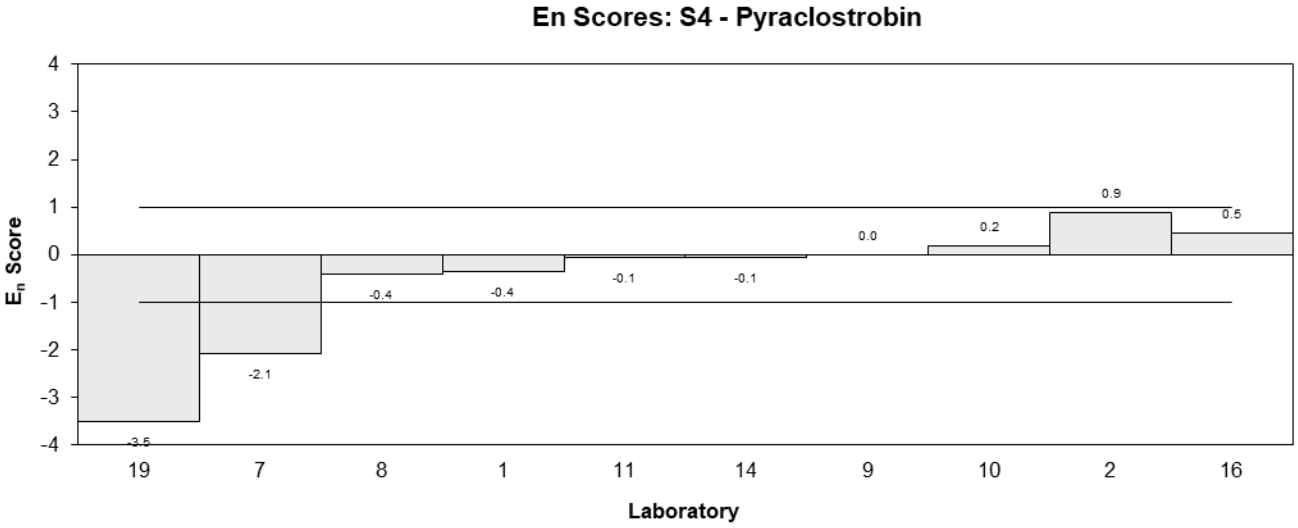

En Scores: S4 - Pyraclostrobin
En Score
Laboratory
19 7 8 1 11 14 9 10 2 16
-3.5
-2.1
-0.4
-0.4
-0.1
-0.1
0.0
0.2
0.9
0.5

Figure 18

# 6 DISCUSSION OF RESULTS

## 6.1 Assigned Value

The assigned values for Sample S1 bifenthrin, buprofezin, chlorpyrifos, endosulfan sulfate, imazalil and pirimicarb, and Sample S2 endosulfan sulfate and pirimicarb, 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 purity of the CRMs used as the reference standards.

The assigned values for all other scored analytes were the robust averages of participants' results. The robust averages and associated expanded uncertainties were calculated using the procedure described in ISO 13528:2022.[7] Results less than 50% and greater than 150% of the robust average were removed before the calculation of the assigned value.[3,4] The calculation of the expanded uncertainty for a robust average is presented in Appendix 3, using Sample S2 metalaxyl 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 S2 permethrin and Sample S4 omethoate, as participants' results were too variable; this variability may have been due to the matrix, mass fraction level, properties of the analyte itself, or a combination of these. For these analytes without assigned values, participants may still compare their results with the descriptive statistics and spiked value as presented in Section 5.

A comparison of the assigned value (or robust average if no assigned value was set) and the spiked value is presented in Table 22. Assigned values for the majority of scored analytes were 90% to 104% of the spiked values, providing good support for the assigned values and further evidence for the stability of these analytes in the test samples. For Sample S4 carbendazim, the recovery was slightly lower at 72%, however there was a very good consensus between participants' results and so this analyte was also scored.

Table 22 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 | Bifenthrin | 0.293 | 0.299 | 98 |
| | Buprofezin | 0.182 | 0.189 | 96 |
| | Chlorpyrifos | 0.787 | 0.819 | 96 |
| | Endosulfan sulfate | 0.614 | 0.647 | 95 |
| | Imazalil | 0.678 | 0.746 | 91 |
| | Imidacloprid | 0.349 | 0.362 | 96 |
| | Pirimicarb | 0.676 | 0.704 | 96 |
| S2 | Endosulfan sulfate | 0.750 | 0.732 | 102 |
| | Metalaxyl | 0.447 | 0.452 | 99 |
| | Permethrin | *(0.158)* | 0.152 | *(104)* |
| | Pirimicarb | 0.702 | 0.697 | 101 |

| Sample | Analyte | Assigned Value *(Robust Average)* (mg/kg) | Spiked Value (mg/kg) | Assigned Value *(Robust Average)* / Spiked Value (%) |
|---|---|---|---|---|
| S3 | Chlorpyrifos | 0.099 | 0.110 | 90 |
| | Imidacloprid | 0.0462 | 0.0489 | 94 |
| | Linuron | 1.14 | 1.10 | 104 |
| S4 | Carbendazim | 0.131 | 0.181 | 72 |
| | Omethoate | *(1.44)* | 1.91 | *(75)* |
| | Pyraclostrobin | 1.12 | 1.11 | 101 |

### 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 231 numeric results for the analytes of interest in this study, 207 (90%) were reported with an associated expanded MU. Participants used a wide variety of procedures to estimate their uncertainty (Table 3). Two participants reported using the NATA Technical Note 33 as their guide; NATA no longer publishes this document.[12]

Laboratory **13** did not report any uncertainties. This laboratory reported that they were accredited to ISO/IEC 17025.

Laboratories **3**, **12**, **14** and **20** did not report uncertainties for at least one of their reported numeric results. All of these participants also 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 5.3% to 85% 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 207 expanded uncertainties, 29 were less than 15% relative and 17 were greater than 50% relative. The uncertainties reported by Laboratory **5** were all 50% relative or greater.

Uncertainties associated with results returning a satisfactory *z* score but an unsatisfactory $E_n$ 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 0.0959 ± 0.0336 mg/kg, it is recommended to report 0.096 ± 0.034 mg/kg.[10]

### 6.3 *z* Scores

Target SDs equivalent to 15% PCV were used to calculate *z* scores for Samples S1, S2 and S4. Target SDs equivalent to 20% PCV were used to calculate z scores for Sample S3 as herb (parsley) was a new matrix introduced in this study. CVs predicted by the Thompson-Horwitz equation,[8] target SDs (as PCV), and the between-laboratory CVs obtained in this study for scored analytes are presented for comparison in Table 23.

Table 23 Comparison of Thompson-Horwitz CVs, Target SDs, and Between-Laboratory CV

| Sample | Analyte | Assigned Value (mg/kg) | Thompson-Horwitz CV (%) | Target SD (as PCV) (%) | Between-Laboratory CV* (%) |
|---|---|---|---|---|---|
| S1 | Bifenthrin | 0.293 | 19 | 15 | 25 |
| | Buprofezin | 0.182 | 21 | 15 | 19 |
| | Chlorpyrifos | 0.787 | 17 | 15 | 18 |
| | Endosulfan sulfate | 0.614 | 17 | 15 | 21 |
| | Imazalil | 0.678 | 17 | 15 | 19 |
| | Imidacloprid | 0.349 | 19 | 15 | 27 |
| | Pirimicarb | 0.676 | 17 | 15 | 10 |
| S2 | Endosulfan sulfate | 0.750 | 17 | 15 | 28 |
| | Metalaxyl | 0.447 | 18 | 15 | 15 |
| | Pirimicarb | 0.702 | 17 | 15 | 17 |
| S3 | Chlorpyrifos | 0.099 | 22 | 20 | 28 |
| | Imidacloprid | 0.0462 | 22 | 20 | 26 |
| | Linuron | 1.14 | 16 | 20 | 20 |
| S4 | Carbendazim | 0.131 | 22 | 15 | 14 |
| | Pyraclostrobin | 1.12 | 16 | 15 | 23 |

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

Of 201 results for which *z* scores were calculated, 162 (81%) returned $|z| \leq 2.0$, indicating a satisfactory performance.

Laboratories **1**, **2**, **7**, **8**, **9**, **11**, **14** and **19** reported numeric results for all 15 scored analytes. Laboratories **11** and **14** achieved satisfactory *z* scores for all of these analytes.

Satisfactory *z* scores were achieved for all scored analytes reported by Laboratories **10** (7), **13** (5) and **6** (4).

The dispersal of participants' *z* scores is presented graphically by laboratory in Figure 19 and by analyte in Figure 20.

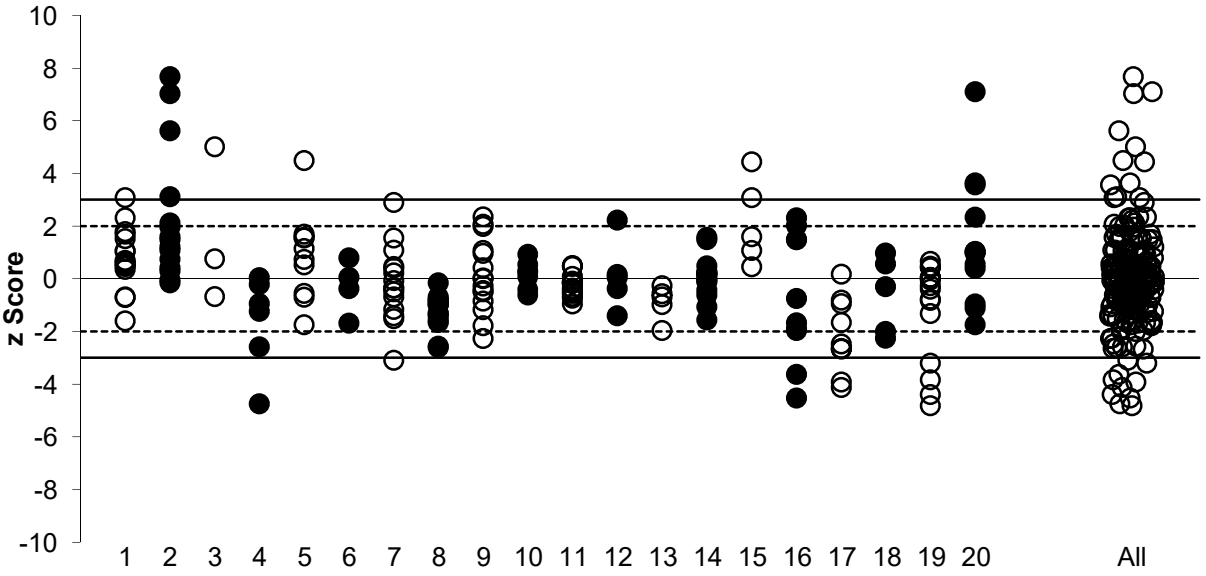


Figure 19 *z* Score Dispersal by Laboratory

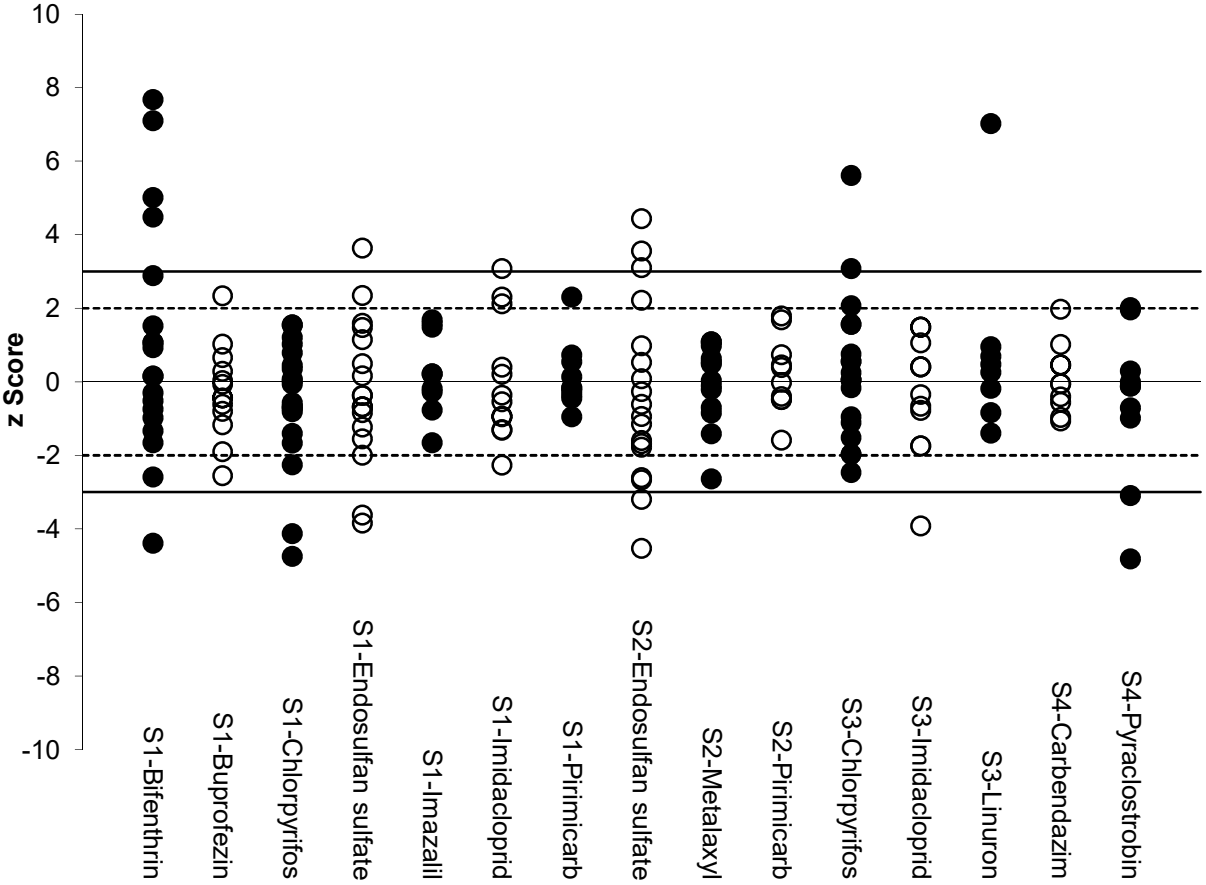
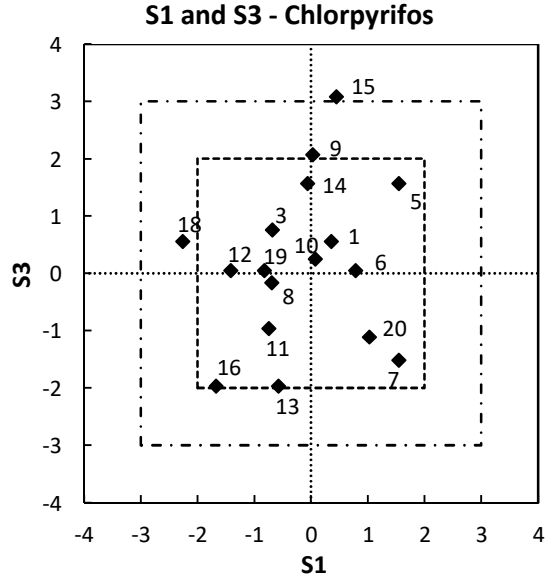


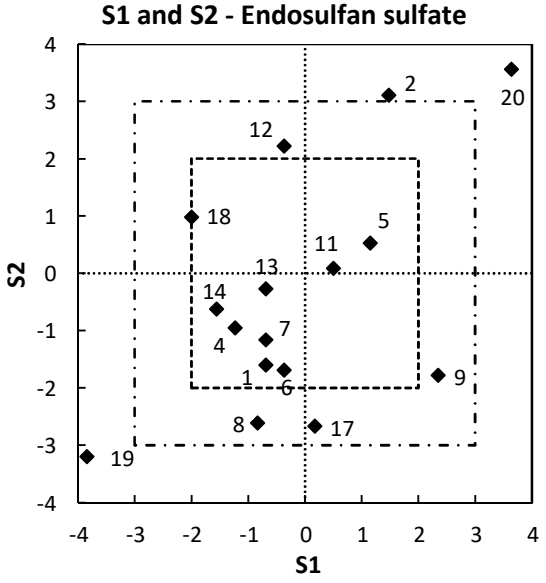

Figure 20 *z* Score Dispersal by Analyte

Scatter plots of *z* scores for chlorpyrifos, endosulfan sulfate, imidacloprid and pirimicarb in different samples are presented in Figures 21 to 24. Scores are predominantly in the upper right and lower left quadrants, indicating that laboratory bias is the major contributor to the variability of results. Points close to the diagonal axis demonstrate excellent repeatability, while points close to the zero demonstrate excellent repeatability and accuracy.




Laboratories 2 and 17 are off-scale.

Figure 21 *z* Score Scatter Plot – Chlorpyrifos in Samples S1 and S3




Laboratories 15 and 16 are off-scale.

Figure 22 *z* Score Scatter Plot – Endosulfan Sulfate in Samples S1 and S2

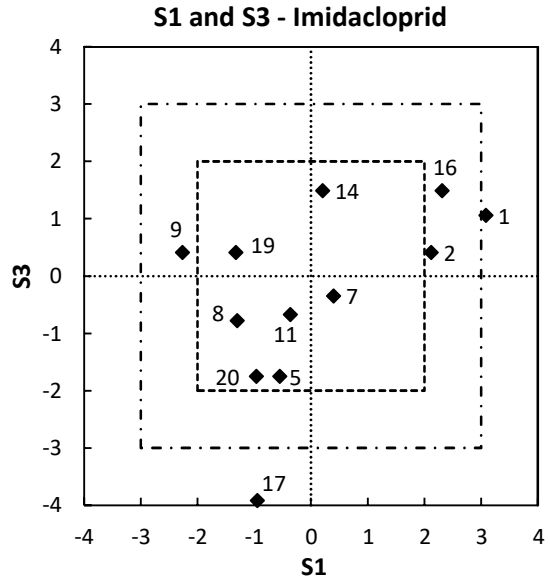



Figure 23 *z* Score Scatter Plot – Imidacloprid in Samples S1 and S3

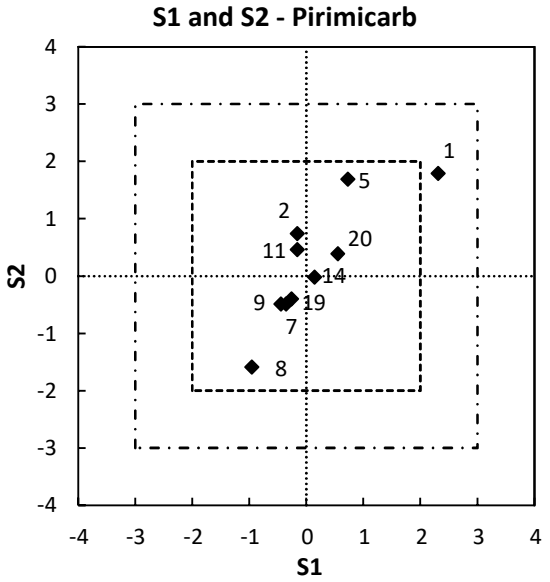



Figure 24 *z* Score Scatter Plot – Pirimicarb in Samples S1 and S2

### 6.4 $E_n$ Scores

$E_n$ scores can be interpreted in conjunction with *z* scores, as an unsatisfactory $E_n$ score can either be caused by an inappropriate 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 201 results for which $E_n$ scores were calculated, 145 (72%) returned $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratory **11** achieved satisfactory $E_n$ scores for all 15 scored analytes in this study.

Satisfactory $E_n$ scores were achieved for all scored analytes reported by Laboratory **10** (7). Laboratory **5** (10) also returned satisfactory $E_n$ scores for all scored analytes reported, though their uncertainties were all 50% relative or greater, which may be not fit for purpose.

The dispersal of participants' $E_n$ scores is presented graphically by laboratory in Figure 25. $E_n$ scores greater than 10 or less than -10 have been plotted at 10 and -10 respectively.

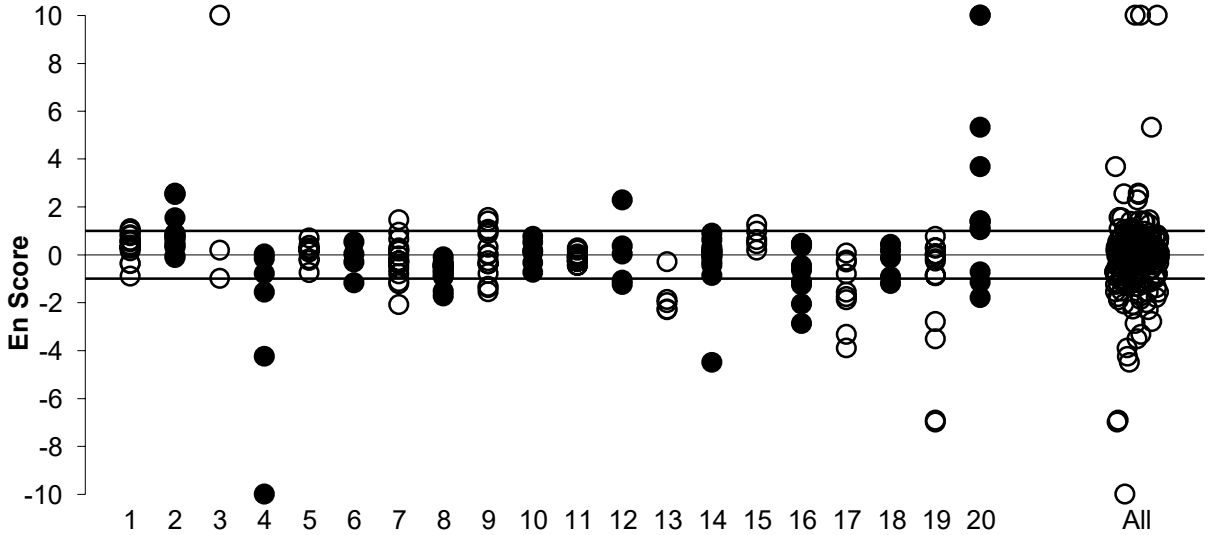



Figure 25 $E_n$ Score Dispersal by Laboratory

## 6.5 False Negatives

Table 24 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, or if no value was reported.

Table 24 False Negatives

| Lab. Code | Sample | Analyte | Assigned Value *(Robust Average)* (mg/kg) | Spiked Value (mg/kg) | Result* (mg/kg) |
|---|---|---|---|---|---|
| 3 | S1 | Endosulfan sulfate | 0.614 | 0.647 | NR |
| | S2 | Endosulfan sulfate | 0.750 | 0.732 | NR |
| 4 | S3 | Chlorpyrifos | 0.099 | 0.110 | NR |
| 13 | S1 | Buprofezin | 0.182 | 0.189 | NR |
| | | Imazalil | 0.678 | 0.746 | NR |
| | | Imidacloprid | 0.349 | 0.362 | NR |
| | | Pirimicarb | 0.676 | 0.704 | NR |
| | S2 | Metalaxyl | 0.447 | 0.452 | NR |
| | | Permethrin | *(0.158)* | 0.152 | NR |
| | | Pirimicarb | 0.702 | 0.697 | NR |
| | S3 | Imidacloprid | 0.0462 | 0.0489 | NR |
| | | Linuron | 1.14 | 1.10 | NR |
| | S4 | Carbendazim | 0.131 | 0.181 | NR |
| | | Pyraclostrobin | 1.12 | 1.11 | NR |
| 16 | S4 | Carbendazim | 0.131 | 0.181 | NR |
| 20 | S2 | Permethrin | *(0.158)* | 0.152 | NR |

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

## 6.6 Reporting of Additional Analytes

Three laboratories reported at least one pesticide which was not spiked into the test samples. These results are presented in Table 25.

Table 25 Non-Spiked Analytes Reported by Participants

| Lab. Code | Sample | Analyte | Result (mg/kg) | Uncertainty (mg/kg) | Recovery (%) |
|---|---|---|---|---|---|
| 1 | S3 | Iprodione | 21 | NR | NR |
| 3 | S1 | Chlorothalonil | 0.334 | NR | 137.09 |
| | S2 | Bifenthrin | 0.523 | NR | 82.84 |
| | S2 | Chlorothalonil | 0.274 | NR | 137.09 |
| 11 | S1 | Glyphosate | 0.02 | 0.0039 | 104 |

## 6.7 Incurred Pesticides in Sample S3

The parsley used to prepare Sample S3 was not organically grown. Several participants reported detecting pesticides in both the unspiked and spiked Sample S3. Reported results for incurred pesticides in Sample S3 are summarised in Table 26 for information only.

Table 26 Incurred Pesticides Reported by Participants in Sample S3

| Lab. Code | Analyte | Unspiked S3 Result (mg/kg) | Sample S3 Result (mg/kg) | Sample S3 Uncertainty (mg/kg) | Sample S3 Recovery (%) |
|---|---|---|---|---|---|
| Partial NMI Screen | Chlorothanonil | 0.024 | 0.024 | NR | NR |
| | Chlorthal Dimethyl | 0.010 | 0.011 | NR | NR |
| | Difenoconazole | 0.033 | 0.030 | NR | NR |
| | Permethrin | 0.063 | 0.058 | NR | NR |
| 1 | Chlorothalonil | NR | 0.023 | 0.007 | 108 |
| | Difenoconazole | 0.033 | 0.033 | 0.008 | 102 |
| | Dithiocarbamates | 1.7 | 1.7 | 0.51 | 75 |
| | Permethrin | NR | 0.061 | 0.017 | 110 |
| 2 | Chlorothalonil | Detected | 0.11 | 0.046 | 152 |
| | Difenoconazole | Detected | 0.059 | 0.002 | 89 |
| | Permethrin | Detected | 0.2 | 0.048 | 114 |
| 5 | Chlorothalonil | NR | 0.03 | 0.02 | 88 |
| | Permethrin | NR | 0.1 | 0.06 | 75 |
| 7 | Chlorothalonil | Detected | 0.037 | 0.011 | 95 |
| | Dithiocarbamates | NR | 3.0 | 0.60 | 76 |
| | Permethrin | Detected | 0.063 | 0.013 | 100 |
| 8 | Permethrin | 0.0854 | 0.0859 | 0.0301 | 95 |
| 9 | Dithiocarbamates | Detected | 0.52 | 0.093 | 117 |
| | Permethrin | Detected | 0.11 | 0.017 | 72 |
| 10 | Chlorothalonil* | Detected | Detected | NR | NR |
| | Difenoconazole* | Detected | Detected | NR | NR |
| 11 | Difenoconazole* | 0.03 | 0.03 | NR | NR |
| | Metalaxyl* | 0.005 | 0.005 | NR | NR |
| | Permethrin | 0.11 | 0.12 | 0.040 | 97 |
| 14 | Chlorthal Dimethyl* | Detected (<0.01) | Detected (<0.01) | NR | NR |
| | Difenoconazole | Detected | 0.04 | 0.01 | 84 |
| | Permethrin | Detected | 0.11 | 0.02 | 93 |
| 16 | Difenoconazole | NR | 0.06 | 0.04 | 106 |
| | Permethrin | NR | 0.04 | 0.02 | 107 |
| 19 | Permethrin | NR | 0.05 | 0.01 | 87.3 |
| 20 | Chlorothalonil | NR | 0.403 | NR | 147 |

* Reported by the participant as a sample comment only.

## 6.8 Range of Pesticides Analysed by Participants

Participants were provided with a list of potential analytes that could have been spiked into the test samples (Table 1). Of these, 13 different analytes were spiked into the samples for this study, with 4 analytes being spiked into multiple samples. Participants were not required to test for all potential analytes, but were requested to report 'NT' (for 'Not Tested') for pesticides they did not test for. A summary of participants' testing of the spiked pesticides is presented in Table 27.

Laboratories **1**, **2**, **7**, **8**, **9**, **11**, **13**, **14** and **19** reported that they tested for all spiked analytes. The proportion of analytes being tested for by each participant ranged from 23% to 100%. Of the spiked analytes in this study, chlorpyrifos was tested for by the highest proportion of participants (100%). The proportion of participants testing for each analyte in this study ranged from 45% to 100%.

Table 27 Summary of Pesticides Analysed by Participants

| Lab. Code / Analyte | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | Proportion of Participants (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Bifenthrin | ✓ | ✓ | ✓ | ✓ | ✓ | NT | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | 95 |
| Buprofezin | ✓ | ✓ | NT | ✓ | NT | NT | ✓ | ✓ | ✓ | ✓ | ✓ | NT | ✓ | ✓ | NT | ✓ | ✓ | NT | ✓ | ✓ | 70 |
| Carbendazim | ✓ | ✓ | NT | NT | NT | NT | ✓ | ✓ | ✓ | ✓ | ✓ | NT | ✓ | ✓ | NT | ✓ | NT | NT | ✓ | ✓ | 60 |
| Chlorpyrifos | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | 100 |
| Endosulfan sulfate | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | NT | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | 95 |
| Imazalil | ✓ | ✓ | NT | NT | NT | NT | ✓ | ✓ | ✓ | NT | ✓ | NT | ✓ | ✓ | NT | ✓ | NT | NT | ✓ | NT | 50 |
| Imidacloprid | ✓ | ✓ | NT | NT | ✓ | NT | ✓ | ✓ | ✓ | NT | ✓ | NT | ✓ | ✓ | NT | ✓ | ✓ | NT | ✓ | ✓ | 65 |
| Linuron | ✓ | ✓ | NT | NT | NT | NT | ✓ | ✓ | ✓ | NT | ✓ | NT | ✓ | ✓ | NT | NT | NT | NT | ✓ | NT | 45 |
| Metalaxyl | ✓ | ✓ | NT | ✓ | ✓ | NT | ✓ | ✓ | ✓ | ✓ | ✓ | NT | ✓ | ✓ | NT | NT | ✓ | NT | ✓ | ✓ | 70 |
| Omethoate | ✓ | ✓ | ✓ | NT | ✓ | ✓ | ✓ | ✓ | ✓ | NT | ✓ | ✓ | ✓ | ✓ | NT | NT | NT | NT | ✓ | ✓ | 70 |
| Permethrin | ✓ | ✓ | ✓ | ✓ | ✓ | NT | ✓ | ✓ | ✓ | NT | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | 90 |
| Pirimicarb | ✓ | ✓ | NT | NT | ✓ | NT | ✓ | ✓ | ✓ | NT | ✓ | NT | ✓ | ✓ | NT | NT | NT | NT | ✓ | ✓ | 55 |
| Pyraclostrobin | ✓ | ✓ | NT | NT | NT | NT | ✓ | ✓ | ✓ | ✓ | ✓ | NT | ✓ | ✓ | NT | ✓ | NT | NT | ✓ | NT | 55 |
| Proportion of Analytes (%) | 100 | 100 | 38 | 46 | 62 | 23 | 100 | 100 | 100 | 46 | 100 | 38 | 100 | 100 | 31 | 69 | 54 | 31 | 100 | 77 | 71 |

### 6.9 Fitness for Purpose of Pesticide Results

The Australia New Zealand Food Standards Code specifies MRLs for various pesticides in different food products.[5] Laboratories should be able to identify whether a sample is compliant with the relevant MRL. In particular, a laboratory should not classify a sample as compliant if the pesticide level is actually greater than the MRL, or vice versa. In this study, 12 analytes with assigned values had associated MRLs. Of these, 10 analytes had assigned values with uncertainty that indicated either compliance or non-compliance with the MRL, while 2 analytes had assigned values with uncertainty spanning the MRL. When assessing participants results, non-numeric results have only been considered here if they were a LOR. In some cases, the MRL refers to the sum of a number of different permitted residues (Table 2), and not only the named analyte given here.

For the 10 analytes that were compliant or non-compliant with the MRL based on their assigned value and uncertainty, the majority of participants' results correctly identified compliance or non-compliance. Of 135 results assessed, 102 (76%) gave the correct compliance status inclusive of uncertainty, while 23 (17%) gave conditionally correct compliance statuses (i.e. the result gave the correct compliance status but the uncertainty spanned the MRL).

Laboratories **9** and **14** returned the correct compliance status, and Laboratories **8** and **11** returned either the correct or conditionally correct compliance statuses, for all 10 analytes assessed. Laboratories **10** (6), **13** (3), **15** (3) and **6** (2) returned the correct compliance status for all reported analytes assessed, while Laboratories **5** (7), **16** (7), **12** (3), and **18** (3) returned correct or conditionally correct compliance statuses for all reported analytes assessed.

Figures 26 to 35 show comparisons of the spiked value (SV, when the assigned value was not a reference value), assigned values (AV), participants' results, and MRLs for these assessed analytes.

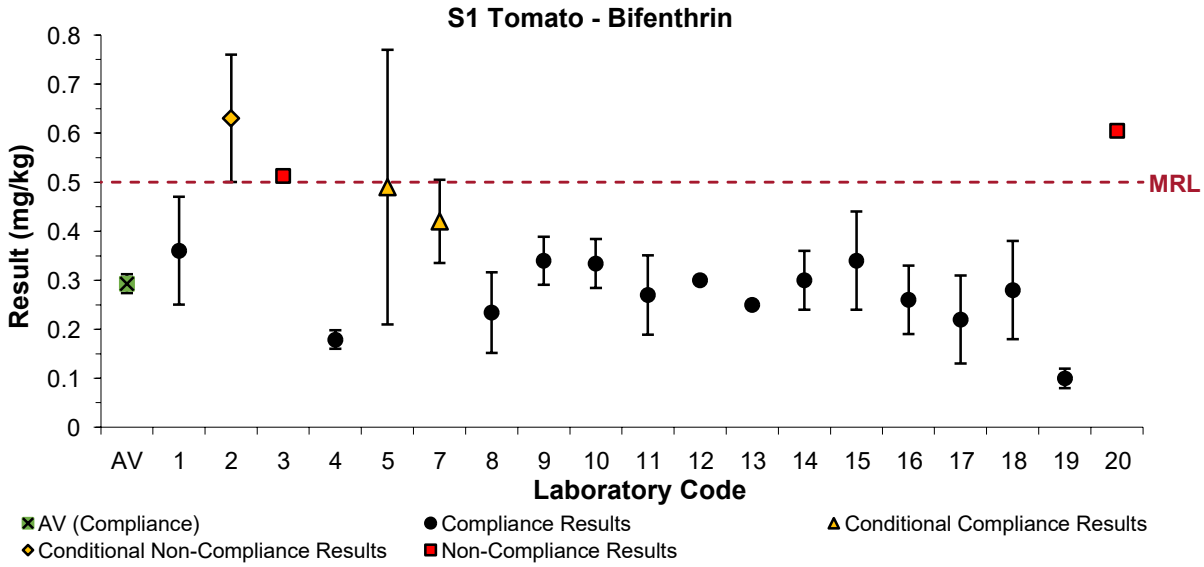



Figure 26 Sample S1 Tomato Bifenthrin Assigned Value, Participant Results and MRL

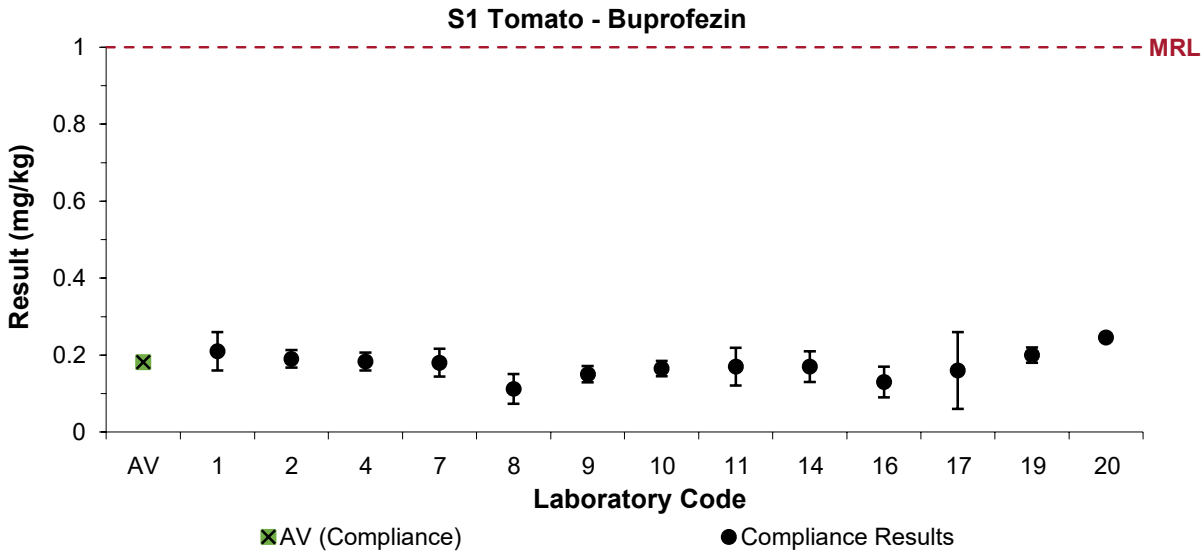



Figure 27 Sample S1 Tomato Buprofezin Assigned Value, Participant Results and MRL

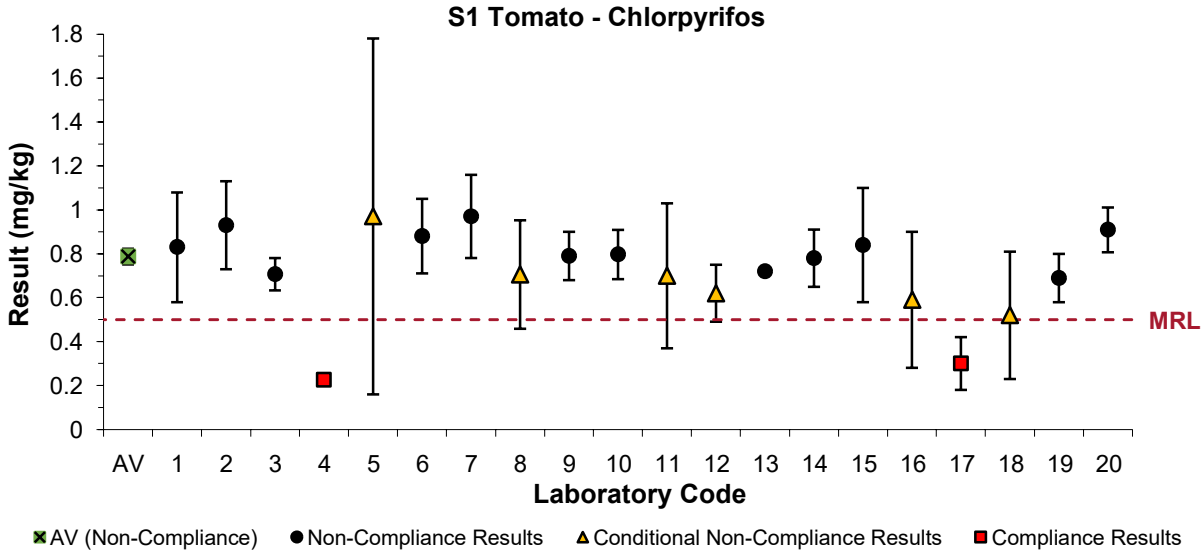



Figure 28 Sample S1 Tomato Chlorpyrifos Assigned Value, Participant Results and MRL

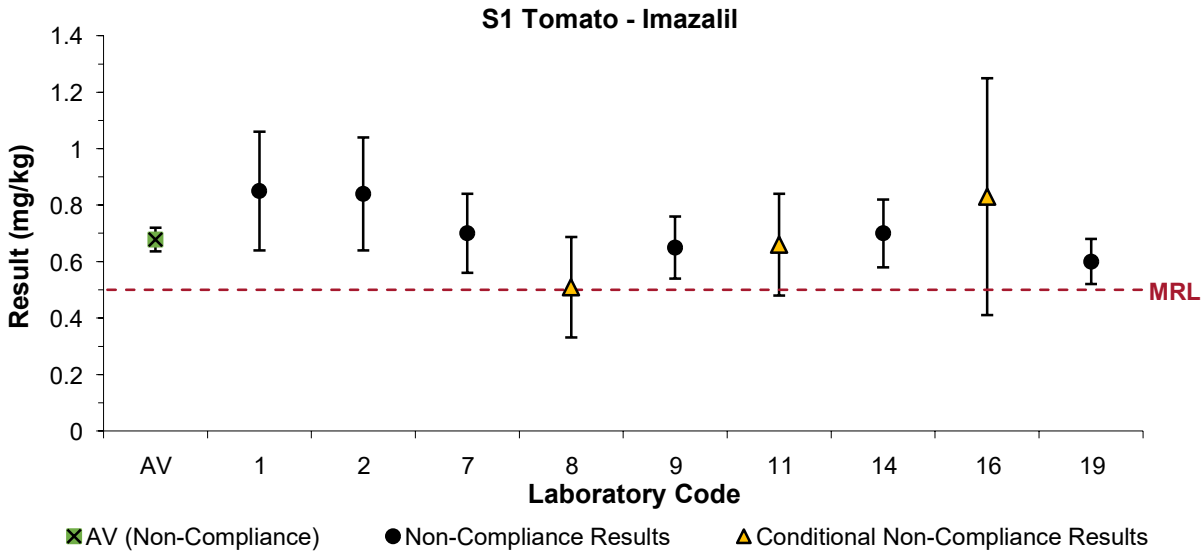



Figure 29 Sample S1 Tomato Imazalil Assigned Value, Participant Results and MRL

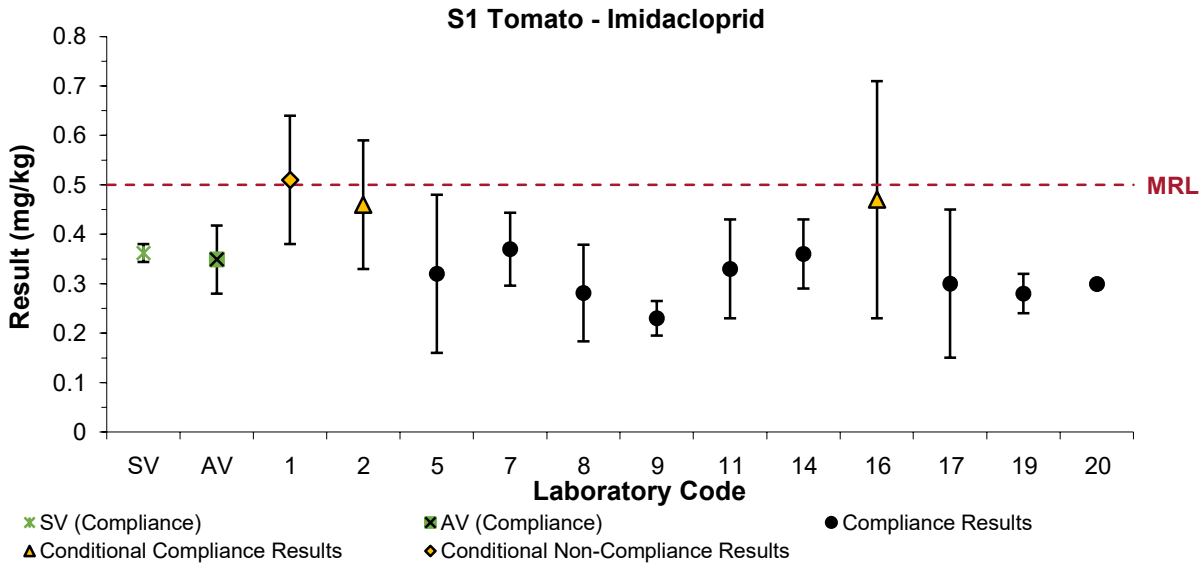



Figure 30 Sample S1 Tomato Imidacloprid Spiked and Assigned Value, Participant Results and MRL

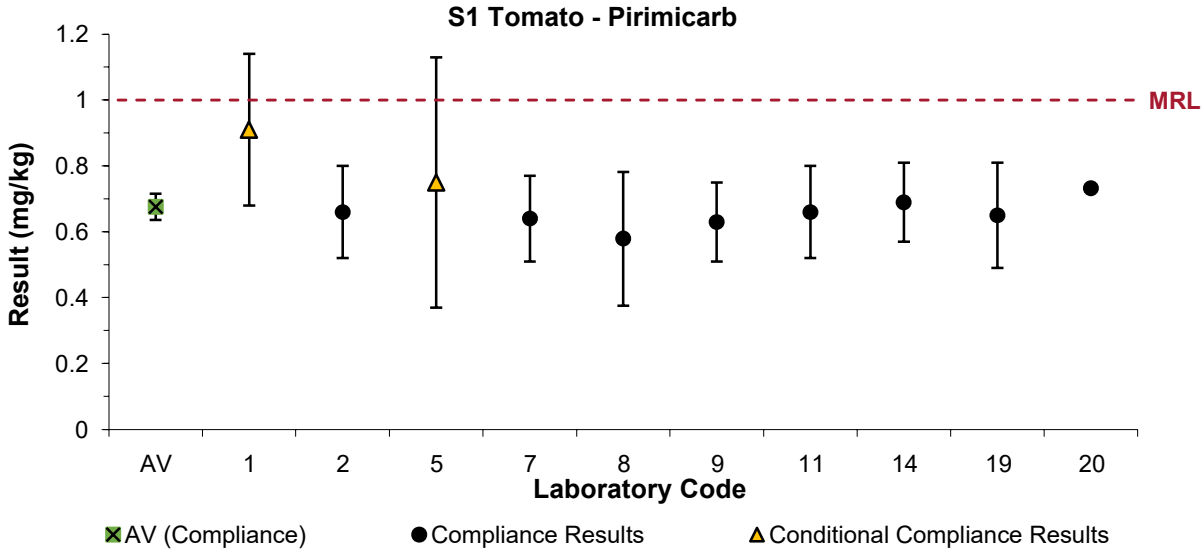



Figure 31 Sample S1 Tomato Pirimicarb Assigned Value, Participant Results and MRL

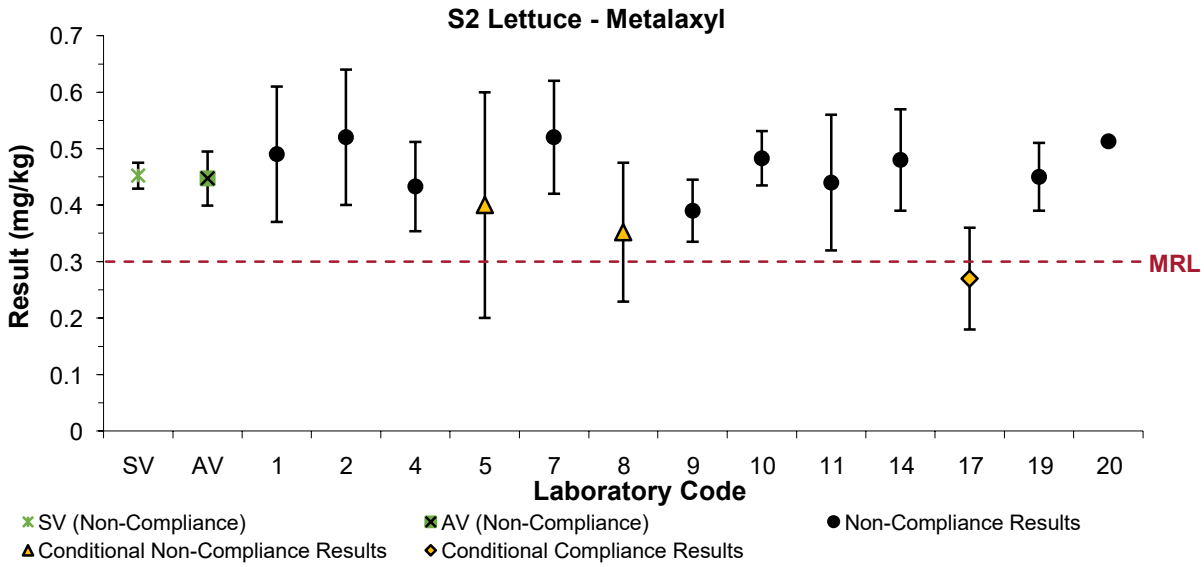



Figure 32 Sample S2 Lettuce Metalaxyl Spiked and Assigned Value, Participant Results and MRL

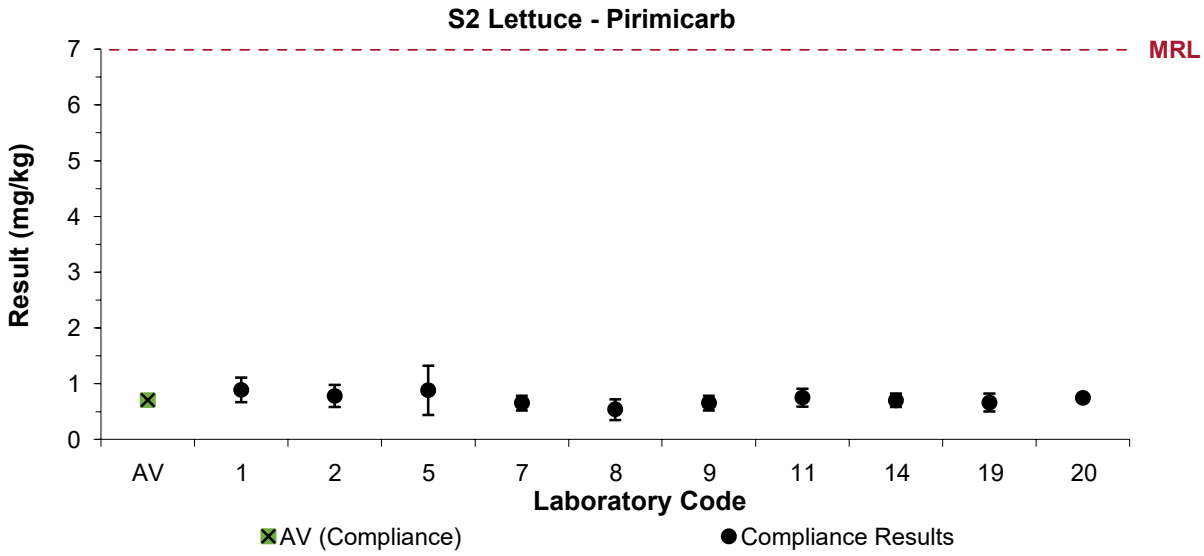



Figure 33 Sample S2 Lettuce Pirimicarb Assigned Value, Participant Results and MRL

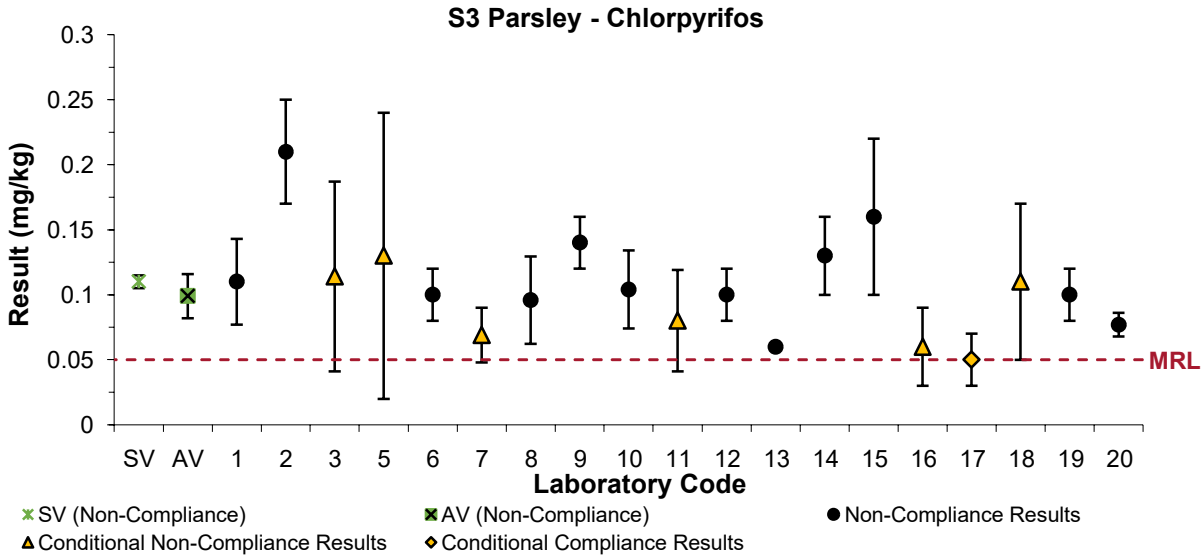



Figure 34 Sample S3 Parsley Chlorpyrifos Spiked and Assigned Value, Participant Results and MRL

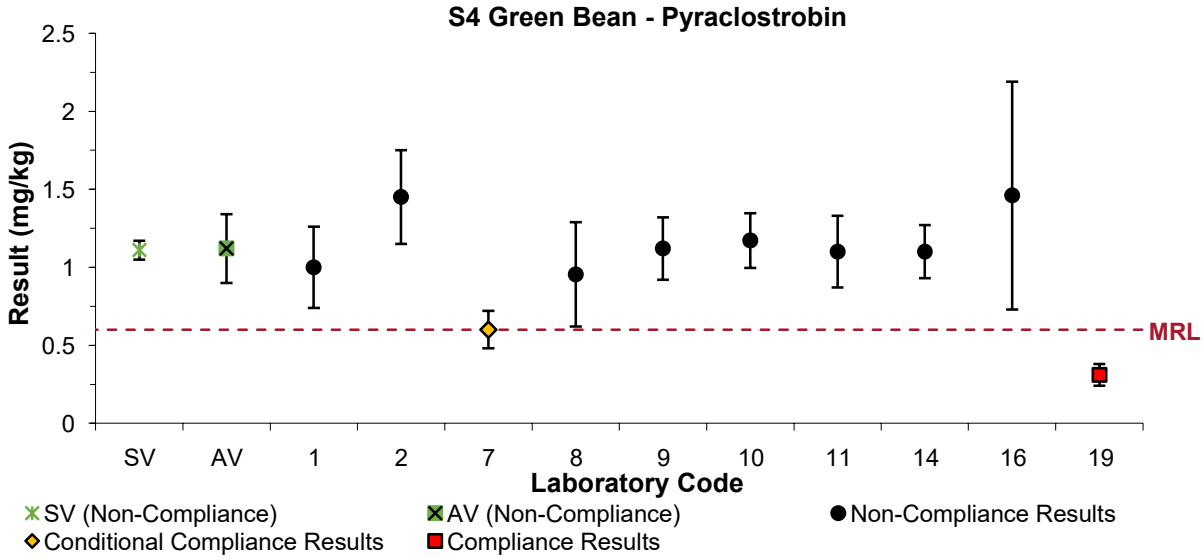



Figure 35 Sample S4 Green Bean Pyraclostrobin Spiked and Assigned Value, Participant Results and MRL

In addition to the above assessed analytes, Sample S3 imidacloprid and linuron had assigned values with uncertainties that spanned the MRL. Figures 36 and 37 show comparisons of the SV, AV, participants' results and MRLs for these analytes.

Sample S3 imidacloprid was prepared with a SV slightly below the MRL, and the AV was also below the MRL (i.e. compliance with the MRL). The majority of participants also reported compliance (including conditional) results. Laboratories **1**, **14** and **16** reported conditional non-compliance results, with their uncertainties all spanning the MRL.

Sample S3 linuron was prepared with a SV slightly above the MRL, and the AV was also above the MRL (i.e. non-compliance with the MRL). The majority of participants also reported non-compliance (including conditional) results. Laboratory **8** reported a conditional compliance result very slightly below the MRL, with uncertainty spanning the MRL. Laboratory **7** reported a compliance result.

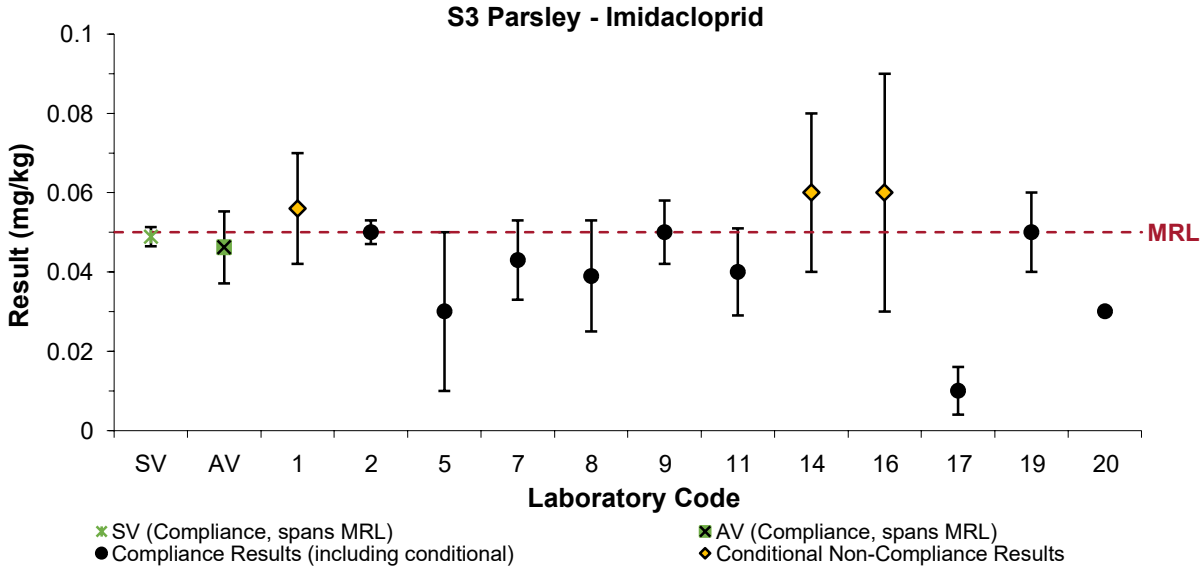



Figure 36 Sample S3 Parsley Imidacloprid Spiked and Assigned Value, Participant Results and MRL

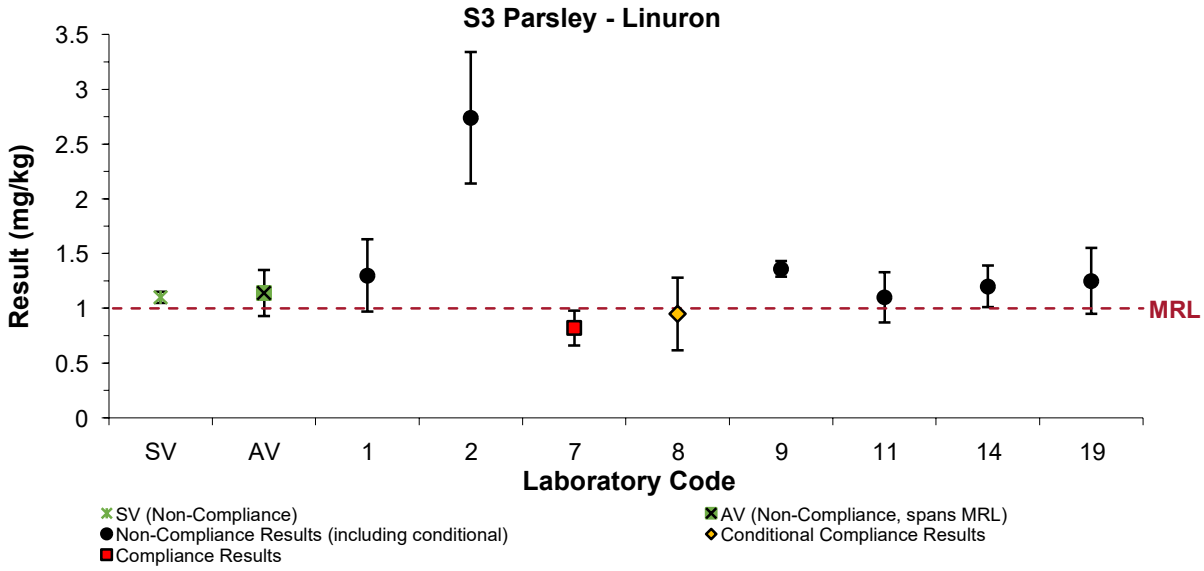



Figure 37 Sample S3 Parsley Linuron Spiked and Assigned Value, Participant Results and MRL

### 6.10 Participants' Analytical Methods

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

Figure 38 shows *z* scores obtained as compared to the sample masses used for analysis. Participants reported using sample sizes between 5 g and 20 g per analysis, with the majority of participants using 10 g. In this PT study there was no evident correlation between the results obtained and sample mass were used.

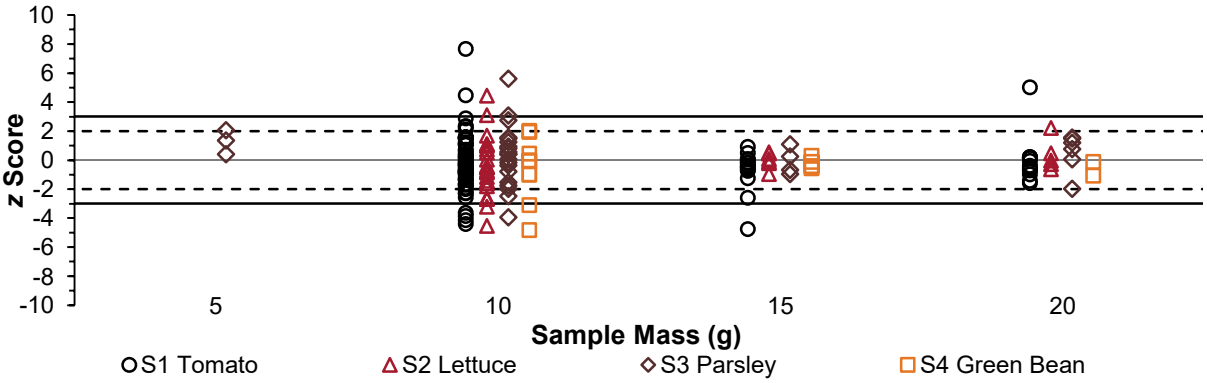



Figure 38 *z* Score vs Sample Mass Used for Analysis

Participants reported using a variety of extraction techniques including solid-liquid extraction (SLE), QuEChERS or other solid phase extractions (SPE), with acetonitrile (ACN), acetone (ACE), hexane (HEX), dichloromethane (DCM), and combinations of these as the extraction solvent. The majority of participants used a clean-up step for analysis, with the use of PSA, C18, $MgSO_4$, carbon (e.g. Envicarb, GCB), 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), nitrogen phosphorus detection (NPD), or liquid chromatography (LC) coupled with MS/MS.

Results compared to methodology used for all analytes are presented in Figures 39 to 55. For scored analytes, participant's results yielding unsatisfactory *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 used was extraction using the QuEChERS procedure,[13] with ACN as the extraction solvent and using LC-MS/MS for analysis.

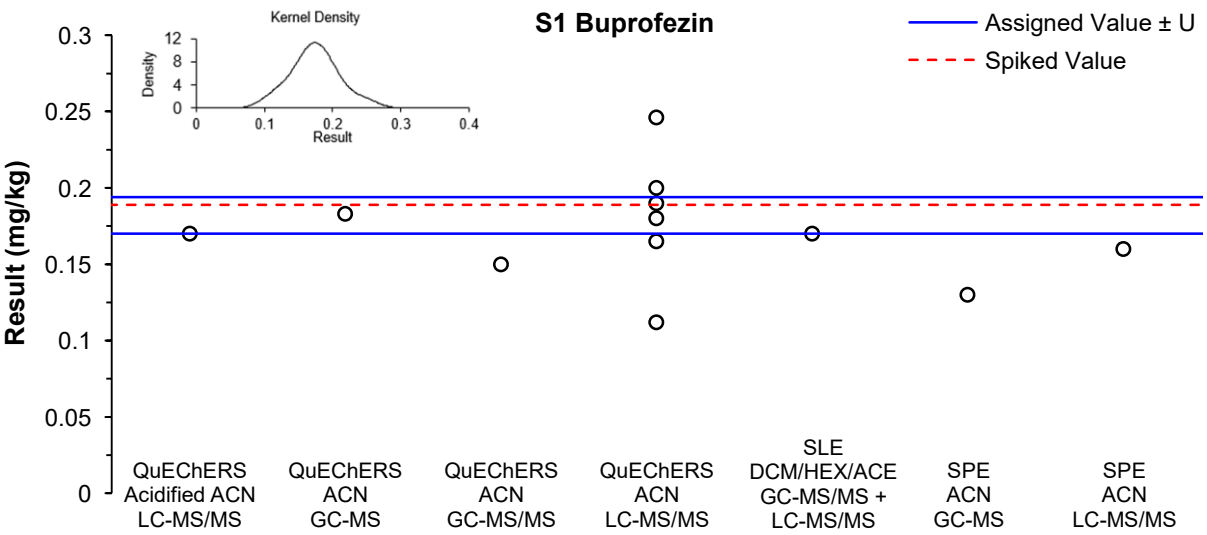



Figure 39 Sample S1 Tomato Buprofezin Result vs Methodology

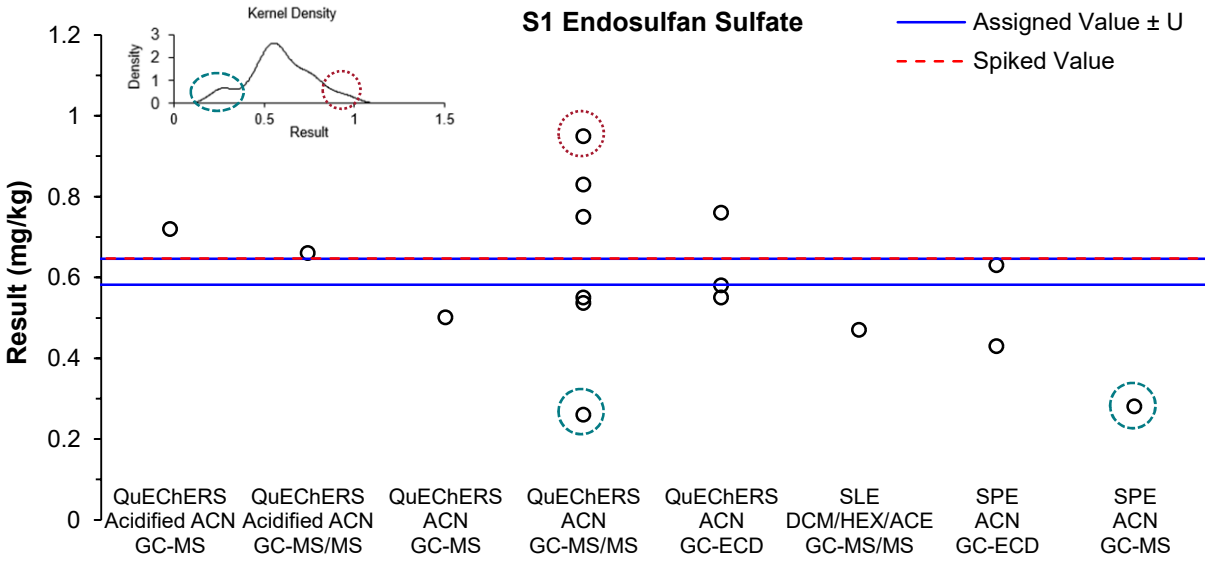



Figure 40 Sample S1 Tomato Endosulfan Sulfate Result vs Methodology

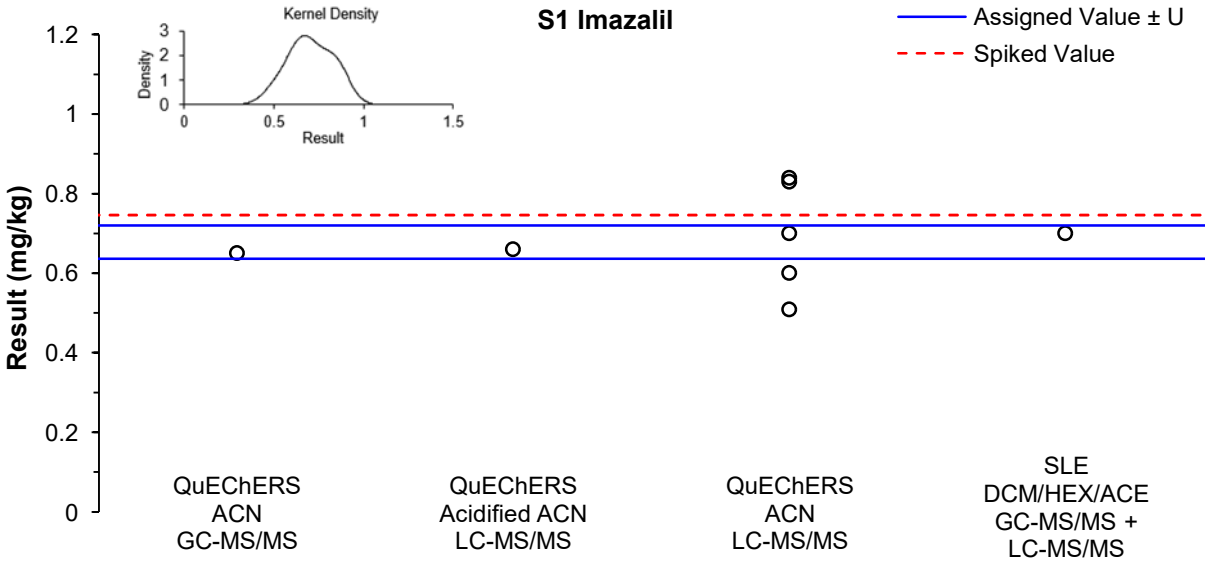



Figure 41 Sample S1 Tomato Imazalil Result vs Methodology

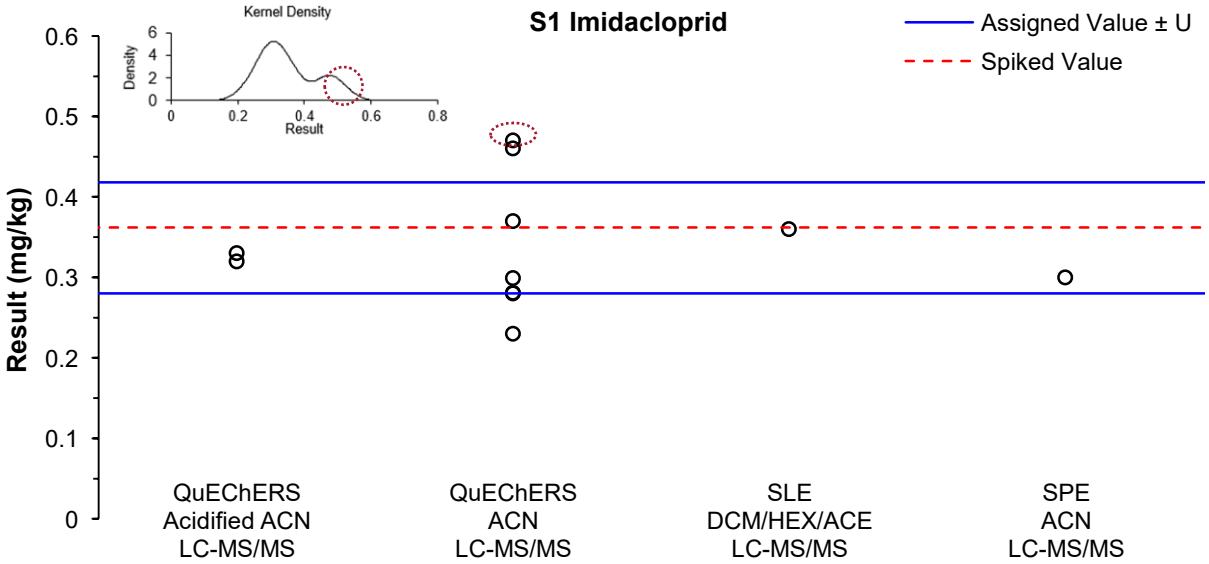



Figure 42 Sample S1 Tomato Imidacloprid Result vs Methodology

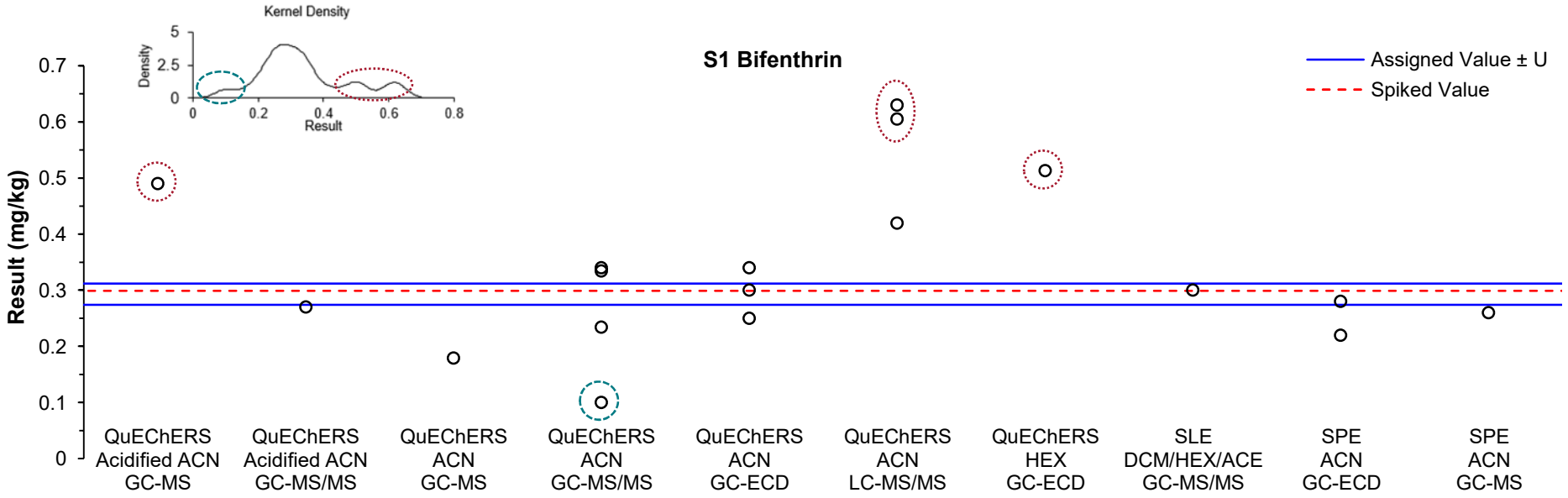



Figure 43 Sample S1 Tomato Bifenthrin Result vs Methodology

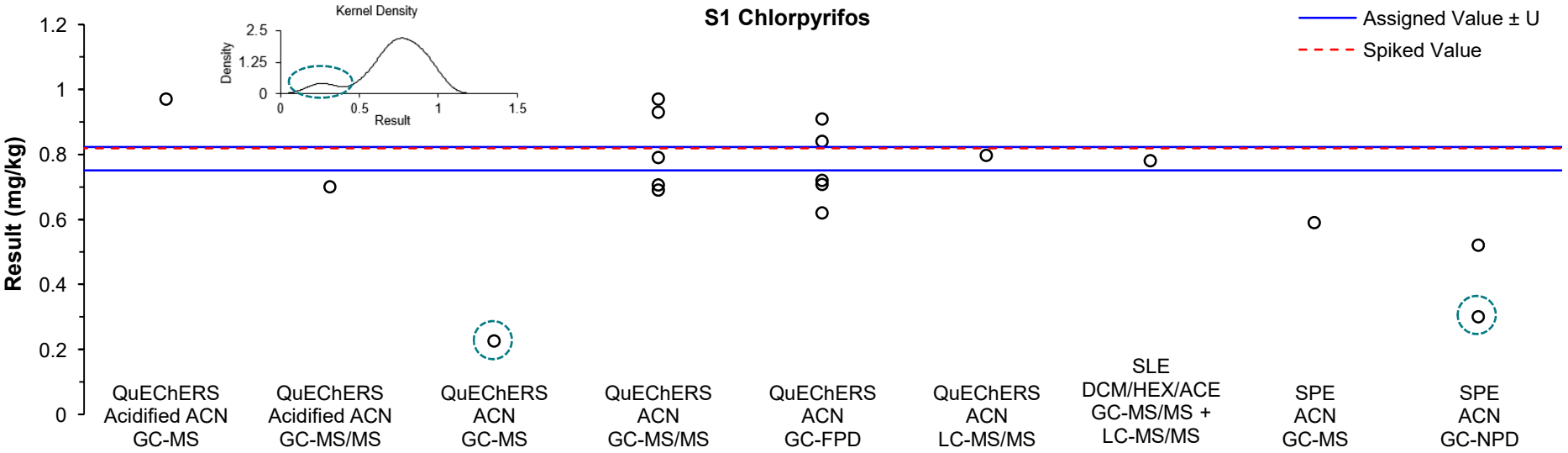



Figure 44 Sample S1 Tomato Chlorpyrifos Result vs Methodology

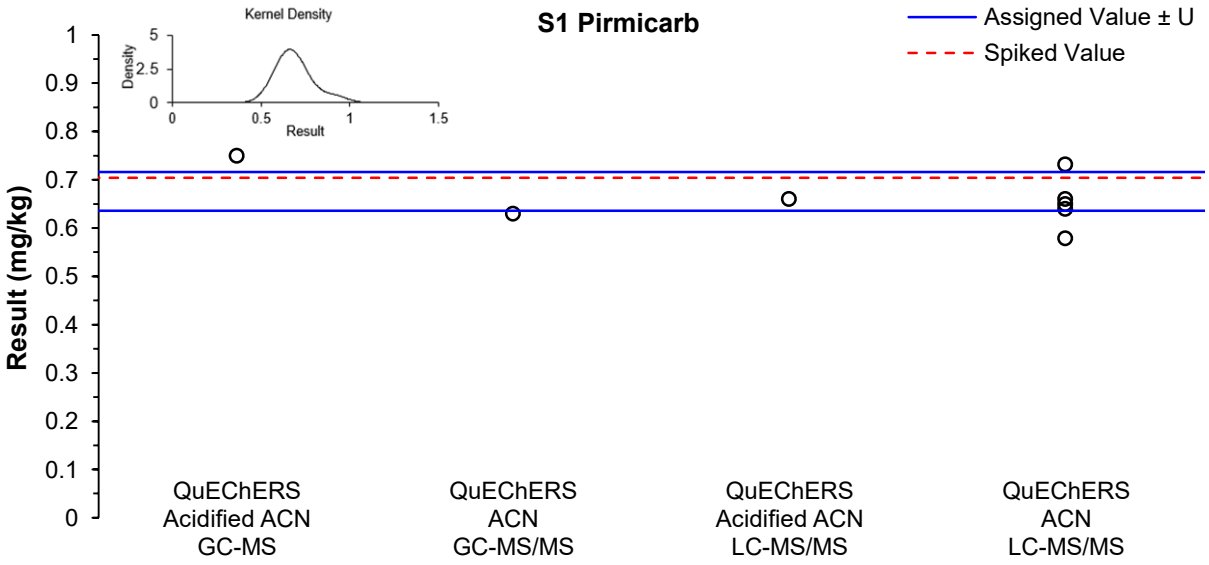



Figure 45 Sample S1 Tomato Pirimicarb Result vs Methodology

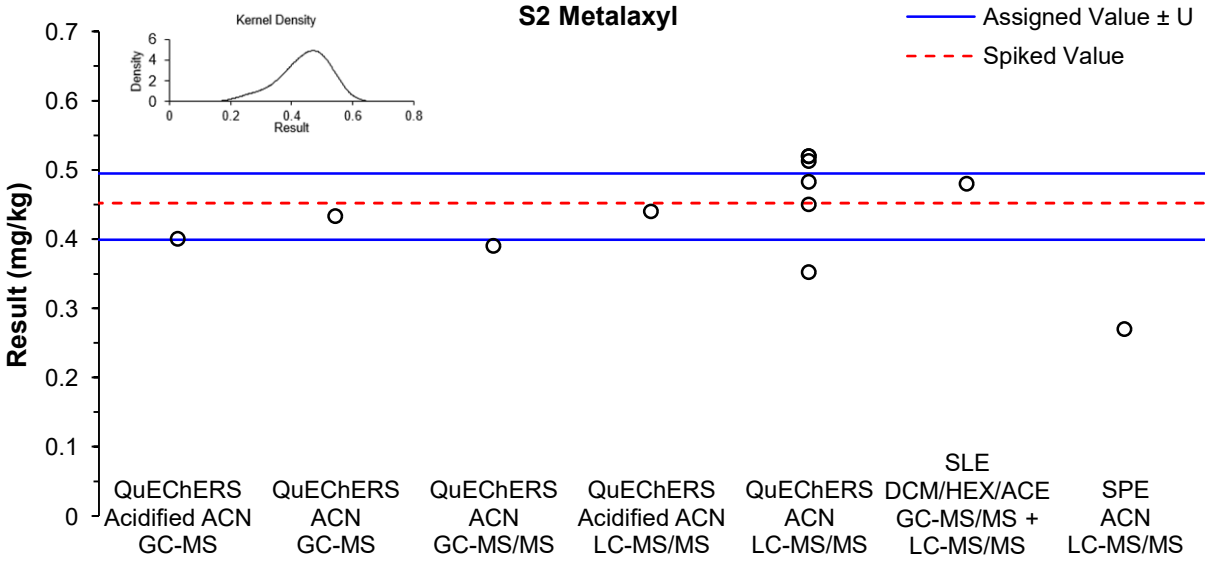



Figure 46 Sample S2 Lettuce Metalaxyl Result vs Methodology

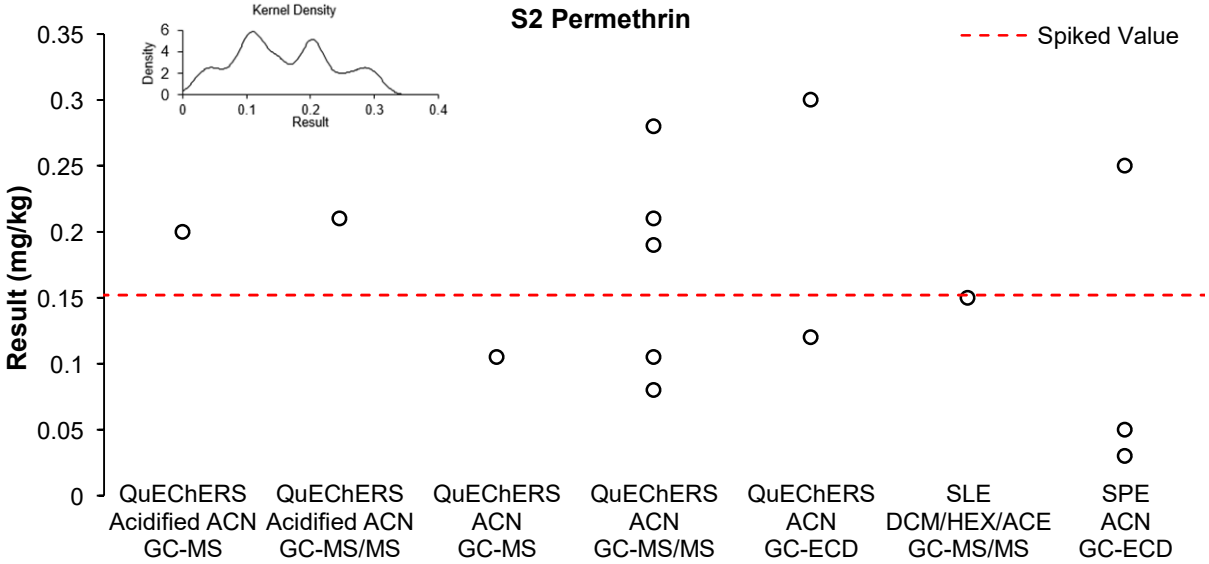



Figure 47 Sample S2 Lettuce Permethrin Result vs Methodology

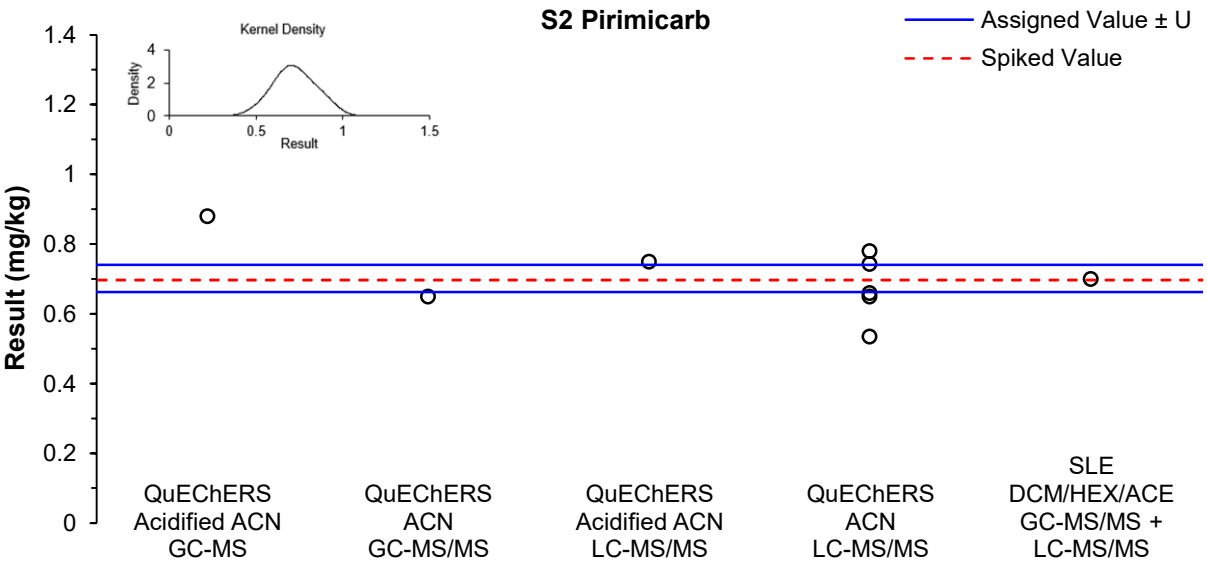



Figure 48 Sample S2 Lettuce Pirimicarb Result vs Methodology

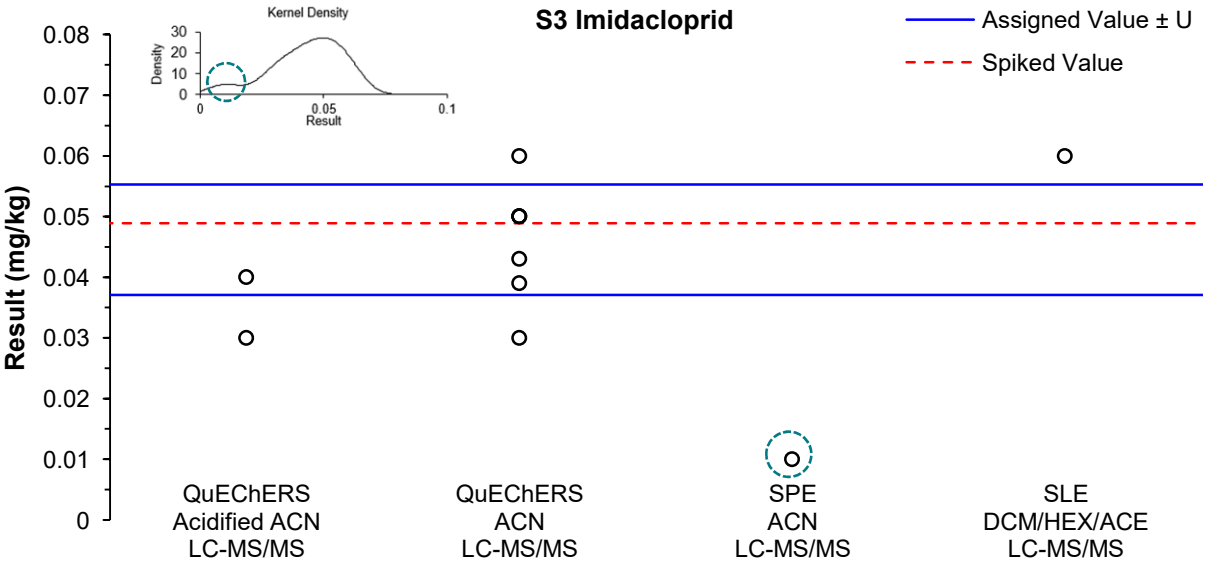



Figure 49 Sample S3 Parsley Imidacloprid Result vs Methodology

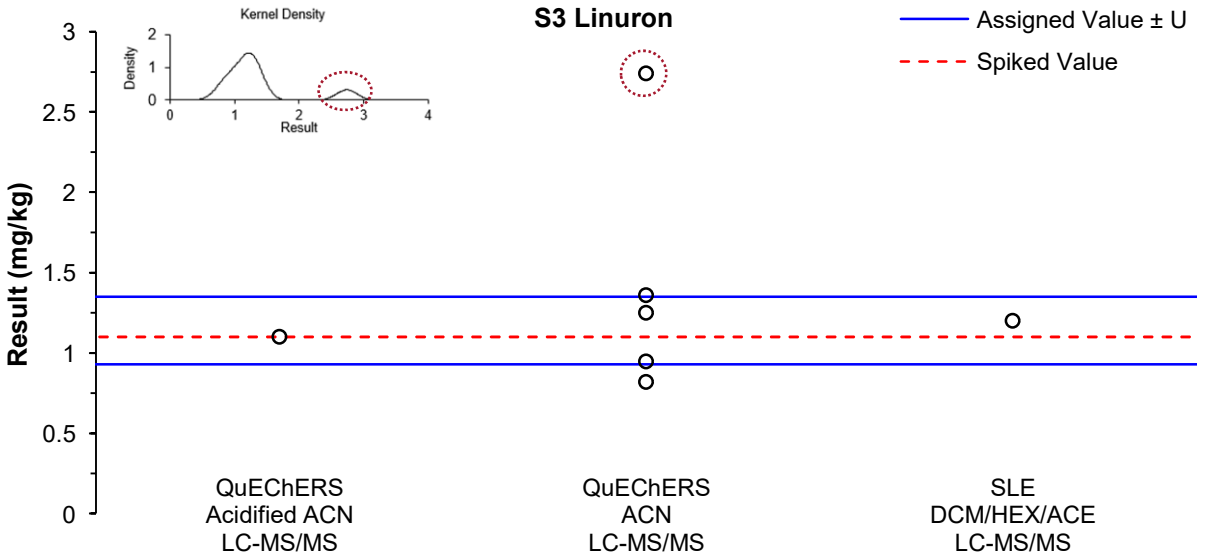



Figure 50 Sample S3 Parsley Linuron Result vs Methodology

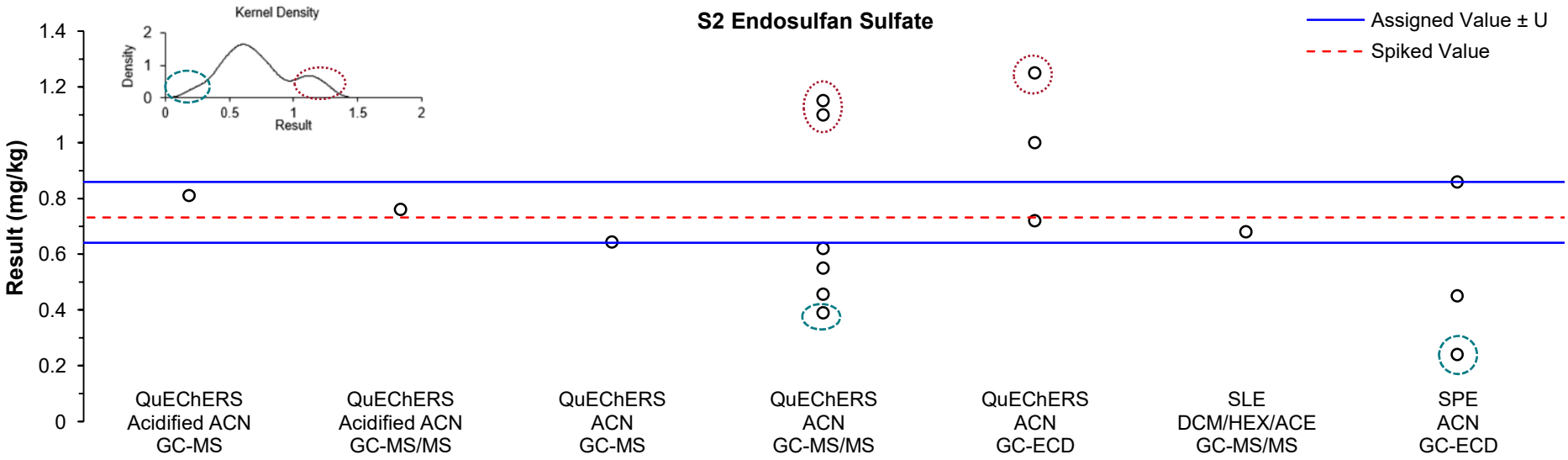



Figure 51 Sample S2 Lettuce Endosulfan Sulfate Result vs Methodology

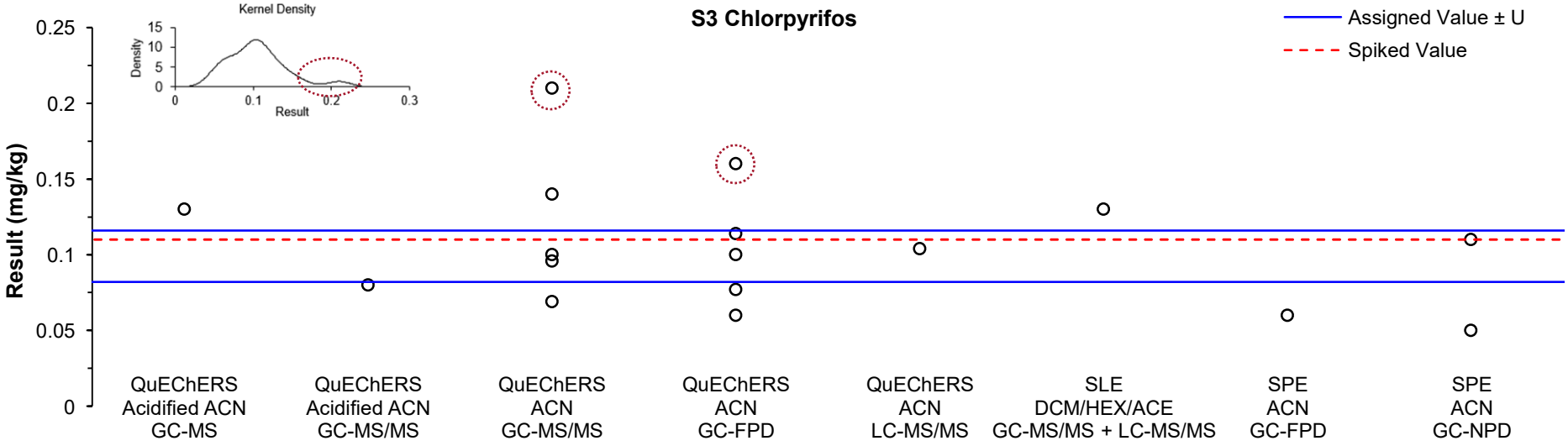



Figure 52 Sample S3 Parsley Chlorpyrifos Result vs Methodology

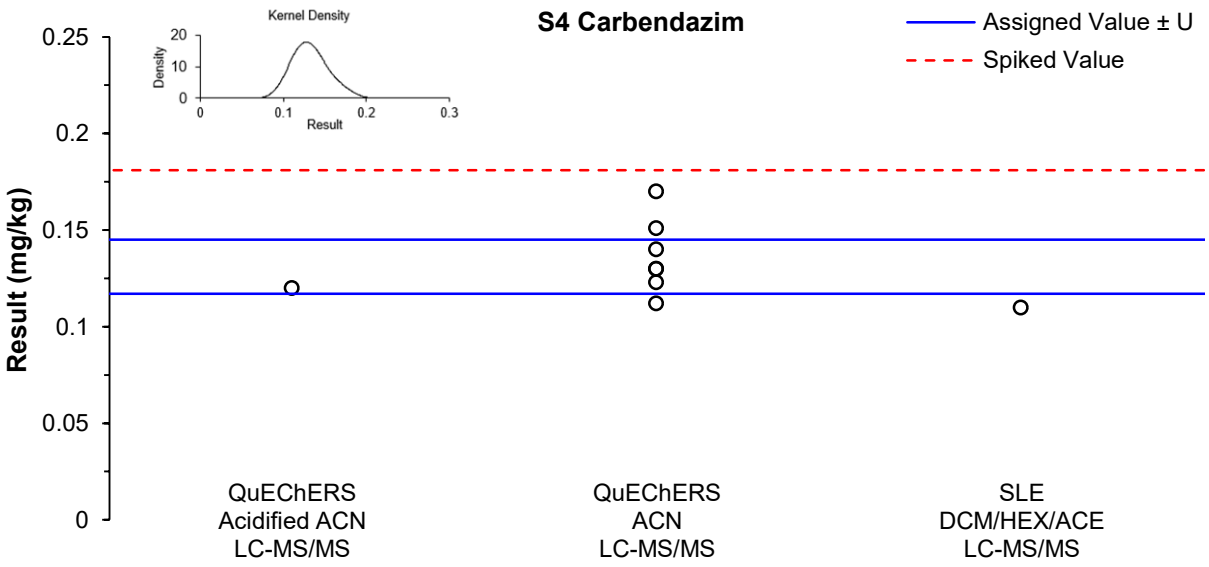



Figure 53 Sample S4 Green Bean Carbendazim Result vs Methodology

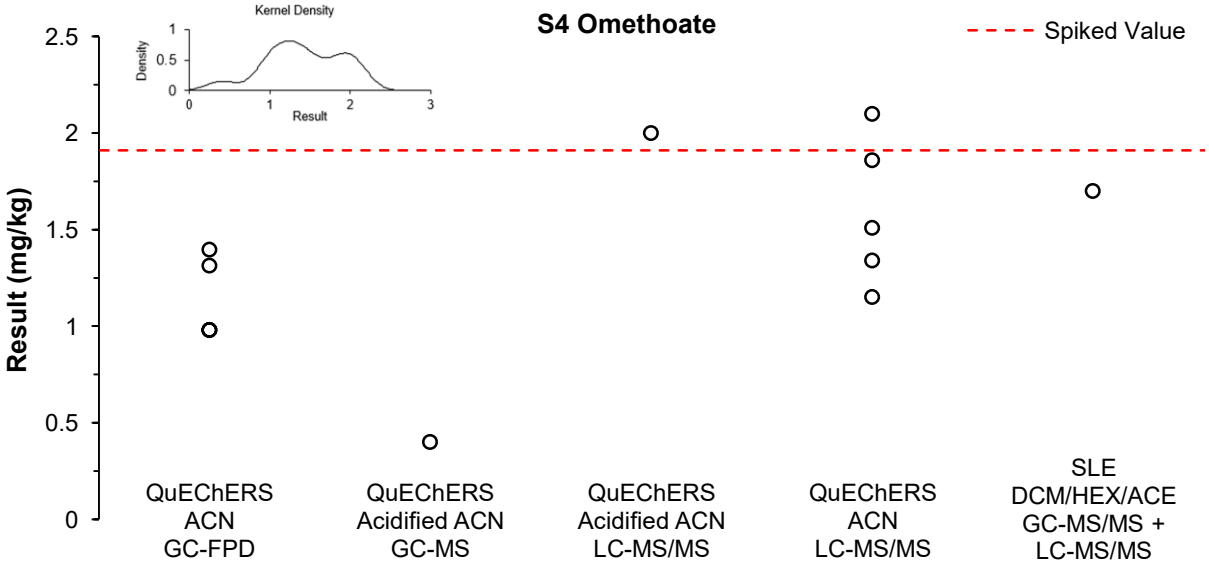



Figure 54 Sample S4 Green Bean Omethoate Result vs Methodology

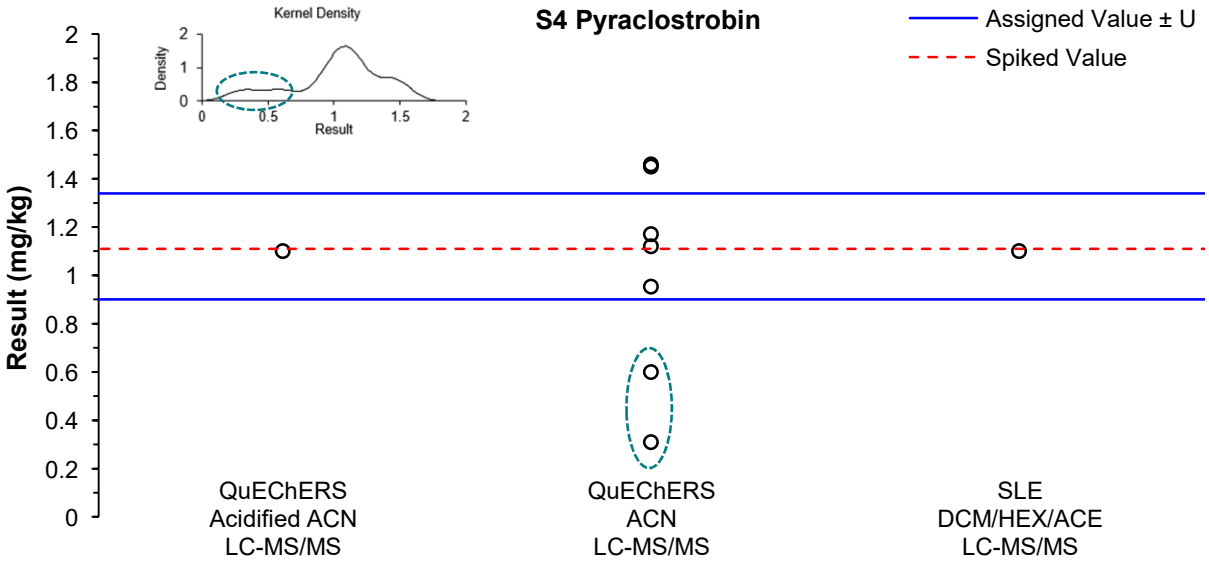



Figure 55 Sample S4 Green Bean Pyraclostrobin Result vs Methodology

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**, **5**, **7**, **8**, **9**, **10**, **11**, **12**, **14**, **15**, **16**, **17**, **18**, **19** and **20** reported recoveries for at least one analyte of interest in this study, and the recoveries reported were within the range of 31% to 160%. Laboratories **1**, **7**, **13**, **15**, **18** and **19** reported that they corrected their results for recovery.

Participants were also provided with blank samples to be analysed if part of their routine procedures (however were requested to not correct the spiked sample results for any analytes detected in the blank samples). Laboratories **1**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **10**, **11**, **13**, **14**, **15**, **16**, **17**, **18** and **19** reported analysing the blank samples.

### 6.11 Certified Reference Materials (CRM)

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

- Dr. Ehrenstorfer
- AccuStandards
- ISO 17034 certified standards
- Certified or reference compounds from other suppliers
- Laboratory control samples

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]

### 6.12 Effect of Sample Matrix

The samples in this study were purees of tomato (Sample S1), lettuce (Sample S2), parsley (Sample S3) and green bean (Sample S4). A summary of the results reported and satisfactory *z* scores obtained for each matrix is presented in Table 28. The proportion of numeric results reported relative to expected number of results ranged from 57% to 72%, and the proportion of satisfactory *z* scores obtained ranged from 78% to 85%. Tomato had the highest proportion of numeric results reported, while parsley and green bean had the highest proportion of satisfactory *z* scores.

Table 28 Result Comparison by Matrix

| Sample | Matrix | Expected Number of Results | Numeric Results Reported | *z* Scores | Satisfactory *z* Scores |
|---|---|---|---|---|---|
| S1 | Tomato | 140 | 101 (72%) | 101 | 80 (79%) |
| S2 | Lettuce | 80 | 57 (71%) | 41 | 32 (78%) |
| S3 | Parsley | 60 | 39 (65%) | 39 | 33 (85%) |
| S4 | Green Bean | 60 | 34 (57%) | 20 | 17 (85%) |

### 6.13 Summary of Participants' Results and Performances

Summaries of participants' results and performances for scored analytes in this PT study are presented in Tables 29 and 30, and Figure 56.

Table 29 Summary of Participants' Sample S1 Results*

| Lab. Code | Sample S1 | | | | | | |
|---|---|---|---|---|---|---|---|
| | Bifenthrin | Buprofezin | Chlorpyrifos | Endosulfan sulfate | Imazalil | Imidacloprid | Pirimicarb |
| AV | 0.293 | 0.182 | 0.787 | 0.614 | 0.678 | 0.349 | 0.676 |
| HV | 0.295 | 0.182 | 0.784 | 0.616 | 0.684 | 0.366 | 0.678 |
| SV | 0.299 | 0.189 | 0.819 | 0.647 | 0.746 | 0.362 | 0.704 |
| 1 | 0.36 | 0.21 | 0.83 | 0.55 | 0.85 | 0.51 | 0.91 |
| 2 | 0.63 | 0.19 | 0.93 | 0.75 | 0.84 | 0.46 | 0.66 |
| 3 | 0.513 | NT | 0.707 | NR | NT | NT | NT |
| 4 | 0.179 | 0.183 | 0.226 | 0.501 | NT | NT | NT |
| 5 | 0.49 | NT | 0.97 | 0.72 | NT | 0.32 | 0.75 |
| 6 | NT | NT | 0.88 | 0.58 | NT | NT | NT |
| 7 | 0.42 | 0.18 | 0.97 | 0.55 | 0.70 | 0.37 | 0.64 |
| 8 | 0.234 | 0.112 | 0.706 | 0.537 | 0.509 | 0.281 | 0.579 |
| 9 | 0.34 | 0.15 | 0.79 | 0.83 | 0.65 | 0.23 | 0.63 |
| 10 | 0.334 | 0.165 | 0.797 | NT | NT | NT | NT |
| 11 | 0.27 | 0.17 | 0.70 | 0.66 | 0.66 | 0.33 | 0.66 |
| 12 | 0.30 | NT | 0.62 | 0.58 | NT | NT | NT |
| 13 | 0.25 | NR | 0.72 | 0.55 | NR | NR | NR |
| 14 | 0.3 | 0.17 | 0.78 | 0.47 | 0.70 | 0.36 | 0.69 |
| 15 | 0.34 | NT | 0.84 | 0.76 | NT | NT | NT |
| 16 | 0.26 | 0.13 | 0.59 | 0.28 | 0.83 | 0.47 | NT |
| 17 | 0.22 | 0.16 | 0.30 | 0.63 | NT | 0.30 | NT |
| 18 | 0.28 | NT | 0.52 | 0.43 | NT | NT | NT |
| 19 | 0.1 | 0.2 | 0.69 | 0.26 | 0.6 | 0.28 | 0.65 |
| 20 | 0.605 | 0.246 | 0.909 | 0.949 | NT | 0.299 | 0.732 |

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

Table 30 Summary of Participants' Samples S2, S3 and S4 Results*

| Lab. Code | Sample S2 | | | Sample S3 | | | Sample S4 | |
|---|---|---|---|---|---|---|---|---|
| | Endosulfan sulfate | Metalaxyl | Pirimicarb | Chlorpyrifos | Imidacloprid | Linuron | Carbendazim | Pyraclostrobin |
| AV | 0.750 | 0.447 | 0.702 | 0.099 | 0.0462 | 1.14 | 0.131 | 1.12 |
| HV | 0.723 | - | 0.693 | 0.13 | 0.056 | - | - | - |
| SV | 0.732 | 0.452 | 0.697 | 0.110 | 0.0489 | 1.10 | 0.181 | 1.11 |
| 1 | 0.57 | 0.49 | 0.89 | 0.11 | 0.056 | 1.3 | 0.14 | 1.0 |
| 2 | 1.1 | 0.52 | 0.78 | 0.21 | 0.05 | 2.74 | 0.13 | 1.45 |
| 3 | NR | NT | NT | 0.114 | NT | NT | NT | NT |
| 4 | 0.643 | 0.433 | NT | NR | NT | NT | NT | NT |
| 5 | 0.81 | 0.4 | 0.88 | 0.13 | 0.03 | NT | NT | NT |
| 6 | 0.56 | NT | NT | 0.10 | NT | NT | NT | NT |
| 7 | 0.62 | 0.52 | 0.65 | 0.069 | 0.043 | 0.82 | 0.14 | 0.60 |
| 8 | 0.456 | 0.352 | 0.535 | 0.0959 | 0.039 | 0.948 | 0.112 | 0.954 |
| 9 | 0.55 | 0.39 | 0.65 | 0.14 | 0.05 | 1.36 | 0.17 | 1.12 |
| 10 | NT | 0.483 | NT | 0.104 | NT | NT | 0.123 | 1.171 |
| 11 | 0.76 | 0.44 | 0.75 | 0.08 | 0.04 | 1.1 | 0.12 | 1.1 |
| 12 | 1.00 | NT | NT | 0.10 | NT | NT | NT | NT |
| 13 | 0.72 | NR | NR | 0.06 | NR | NR | NR | NR |
| 14 | 0.68 | 0.48 | 0.70 | 0.13 | 0.06 | 1.2 | 0.11 | 1.1 |
| 15 | 1.25 | NT | NT | 0.16 | NT | NT | NT | NT |
| 16 | 0.24 | NT | NT | 0.06 | 0.06 | NT | NR | 1.46 |
| 17 | 0.45 | 0.27 | NT | 0.05 | 0.01 | NT | NT | NT |
| 18 | 0.86 | NT | NT | 0.11 | NT | NT | NT | NT |
| 19 | 0.39 | 0.45 | 0.66 | 0.1 | 0.05 | 1.25 | 0.13 | 0.31 |
| 20 | 1.151 | 0.513 | 0.743 | 0.077 | 0.03 | NT | 0.151 | NT |

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

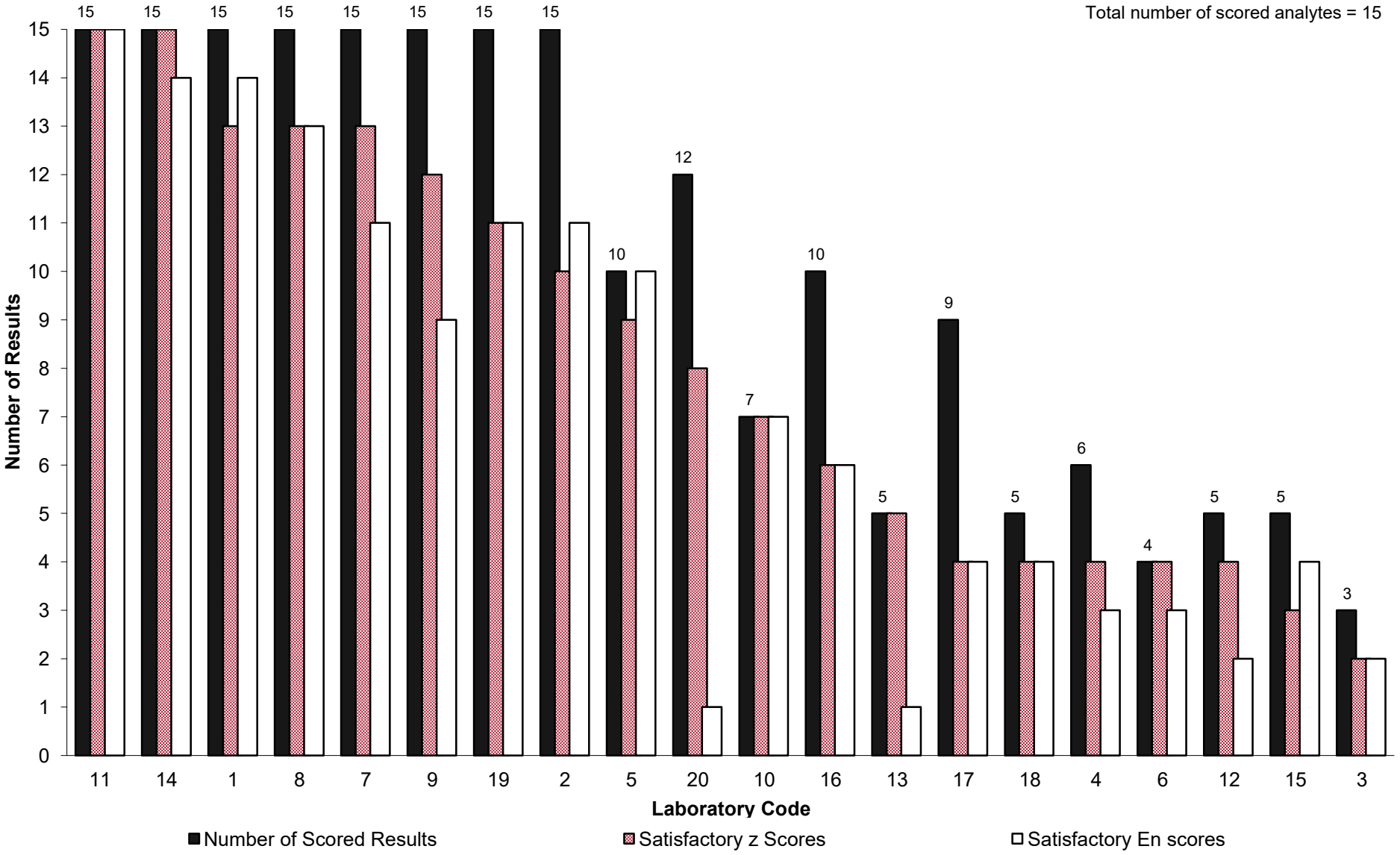



Figure 56 Summary of Participants' Performance

### 6.14 Comparison with Previous Pesticides in Fruit, Vegetables and Herbs PT Studies

A summary of participation and reported results rates in NMI Pesticides in Fruit, Vegetables and Herbs PT studies over the last 10 studies (2015 to 2022) is presented in Figure 57. While the number of spiked analytes per study has increased, and a new matrix (herb) was introduced this year, the numeric results reported by participants have remained fairly steady.

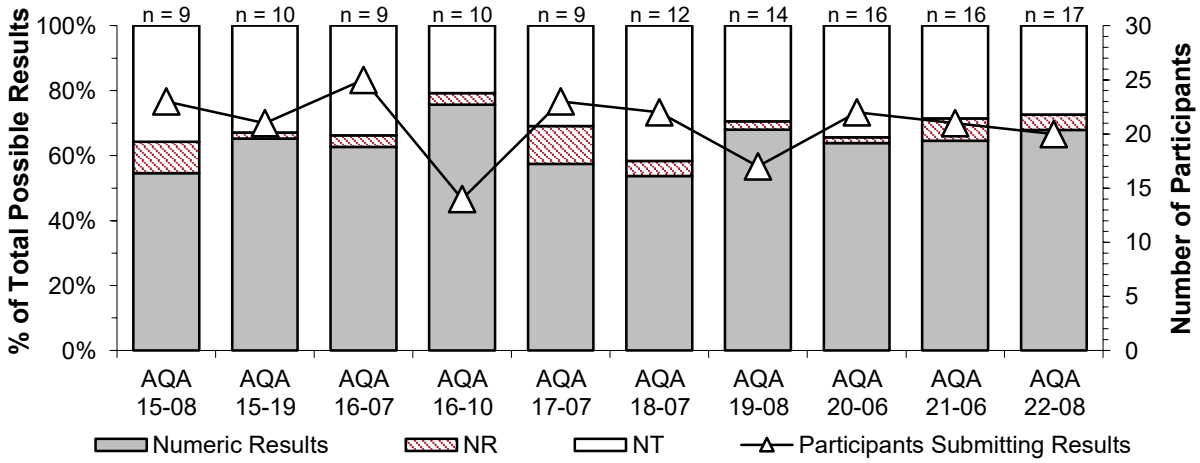



Figure 57 Summary of Participation and Reported Results in NMI Pesticides in Fruit, Vegetables and Herbs PT Studies (n = number of spiked analytes)

A summary of the satisfactory performance (presented as a percentage of the total number of scores for each study) in NMI Pesticides in Fruit, Vegetables and Herbs PT studies over the last 10 studies (2015 to 2022) is presented in Figure 58. The target SD used to calculate *z* scores has been kept constant at 15% PCV, except for the new herb matrix in this study where 20% PCV was used. Over this period, the average proportion of satisfactory scores was 77% for *z* scores and 69% for $E_n$ scores. While each PT study has a different sample set and a different group of participants, taken as a group, the performance over this period has been improving.

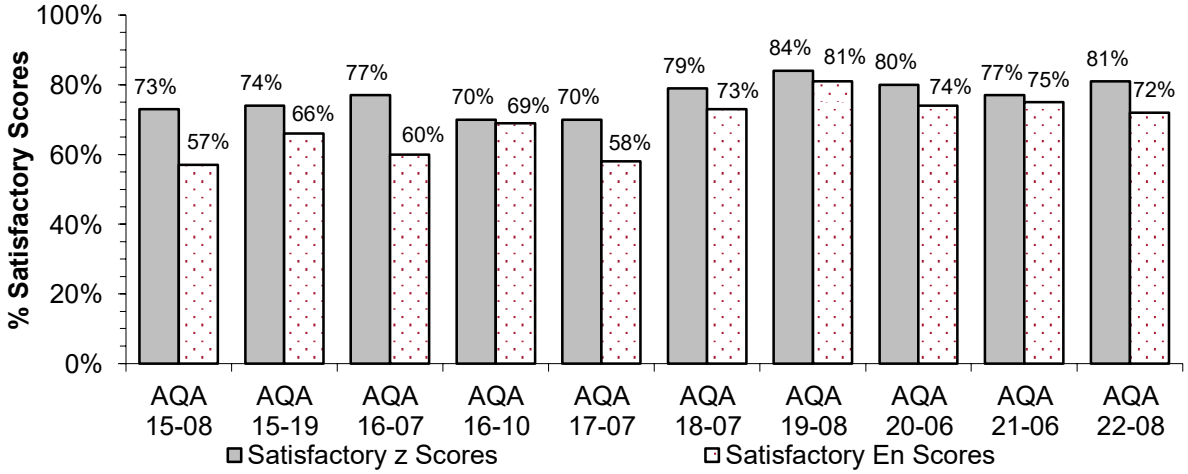



Figure 58 Summary of Participants' Performance in NMI Pesticides in Fruit, Vegetables and Herbs PT Studies

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.

## 7 REFERENCES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## APPENDIX 1 SAMPLE PREPARATION

Tomatoes, lettuce and green beans were bought from a Sydney organic fruit and vegetable wholesaler. Parsley was bought from a Sydney grocery store. The portion of the fruit, vegetables and herbs 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 whole tomato, including the peel, was chopped, pureed and passed through an 850 µm sieve. The sieved puree was continuously stirred while 40 aliquots of at least 100 g were dispensed into 200 mL amber bottles to provide unspiked samples. The remaining puree was supplemented with tomato puree prepared previously using the same process. The puree was spiked with aliquots of each pesticide standard solution. The spiked puree was stirred for at least two hours. Bottles were then dispensed, labelled, shrink-wrapped in plastic film and placed in a freezer.

### Preparation of Sample S2 (Lettuce)

The lettuce was rinsed using tap water and allowed to air dry. It was then chopped, placed in a stainless steel drum, pureed with a stick mixer and passed through an 850 µm sieve. The puree was continuously stirred while 45 aliquots of at least 100 g were dispensed into 200 mL amber bottles to provide unspiked samples. The remaining puree was spiked with aliquots of each pesticide standard solution. The spiked puree was stirred for at least two hours and bottled. Each bottle was then labelled, shrink-wrapped and placed in a freezer.

### Preparation of Sample S3 (Parsley)

The parsley was rinsed with tap water and allowed to dry. It was placed into a stainless steel drum and water was added to assist blending. It was blended using a stick mixer to form a puree which was passed through an 850 µm sieve. The puree was continuously stirred while 40 aliquots of at least 50 g were dispensed into 100 mL amber bottles to provide unspiked samples. The remaining puree was spiked with aliquots of each pesticide standard solution, stirred for at least two hours and bottled. Each bottle was then labelled, shrink-wrapped and placed in a freezer.

### Preparation of Sample S4 (Green Bean)

The green beans were rinsed with tap water and allowed to dry. The ends were cut off the green beans and they were placed in a stainless steel drum and pureed with a stick mixer, with water being added to facilitate blending. The blended green beans were then passed through an 850 µm sieve. After sieving, water was added to the sieved green beans to enable mixing. The resultant 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 aliquots of each pesticide standard solution. The spiked beans were stirred for at least two hours and bottled. Each bottle was then labelled, shrink-wrapped and placed in a freezer.

## APPENDIX 2 REFERENCE VALUES, HOMOGENEITY AND STABILITY

### A2.1 Reference Values

Reference values were obtained for Sample S1 bifenthrin, buprofezin, chlorpyrifos, endosulfan sulfate, imazalil and pirimicarb, and Sample S2 endosulfan sulfate and pirimicarb. Analysis for the provision of these reference values was done by NMI Sydney (Chemical Reference Values).

The standard uncertainties on the mass fraction reference values were estimated in accordance with the ISO GUM,[11] by combining standard uncertainty terms for method precision, weighing of sample, mass fraction in the calibration blends, isotope ratios in standards for analytes where these are relevant, an estimate of potential interference made by comparing the results from primary and confirmatory methods (matrix), and between-batch variation. Samples were analysed in duplicate and under repeatability conditions so that homogeneity checks could be performed (Section A2.2 Homogeneity Assessment), and additional samples were also analysed for transportation short-term stability (Section A2.3 Stability Assessment); the uncertainty terms for these components were also included in the uncertainty budget. Coverage factors (k) were calculated using effective degrees of freedom derived from the Welch-Satterthwaite equation.

#### Methodology

Samples S1 and S2 were analysed by 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 5 g of sample. Matched calibration blends were prepared gravimetrically from the mixed internal standard and aliquots of gravimetrically prepared solutions of pesticide reference materials.

Pesticides were extracted from samples using acidified acetonitrile, magnesium sulfate and sodium acetate (QuEChERS methodology), and extracts subjected to dispersive solid-phase extraction (dSPE) using one of two commercial products, containing PSA/C18EC/$MgSO_4$ (C18) or PSA/Carbon S/$MgSO_4$ (CS).

All analytes were quantitated by analysing diluted dSPE (C18) extracts with one of two 2D-LC-MS/MS methods (primary LC/MS). Buprofezin and imazalil were also quantitated by analysing diluted dSPE (CS) extracts with a third 2D-LC/MS method (confirmatory LC/MS). Further separation of dSPE (C18) extracts using semi-preparative high-pressure liquid chromatography (HPLC) allowed bifenthrin, chlorpyrifos, endosulfan sulfate, imazalil and pirimicarb to be extracted from the HPLC fractions using toluene and quantitated by GC-MS/MS (confirmatory GC/MS).

#### Sample S1 Reference Values

Sample S1 was analysed in four batches: one batch of 8 samples, a homogeneity batch of 10 samples, and two transportation stability (refrigerated and room temperature) batches of 5 samples each. All samples were extracted in duplicate. The first batch of 8 samples, the refrigerated stability, and the reference samples from the room temperature stability were analysed by both the primary and confirmatory methods. Reference values were obtained by averaging batch results.

The reference values obtained for the Sample S1 analytes are presented in Table 31.

Table 31 Reference Values for Sample S1 Tomato

| Analyte | Reference Value (mg/kg) | Expanded Uncertainty (95%) (mg/kg) | Coverage Factor, k (95%) |
|---|---|---|---|
| Bifenthrin | 0.293 | 0.019 | 2.1 |
| Buprofezin | 0.182 | 0.012 | 2.0 |
| Chlorpyrifos | 0.787 | 0.036 | 2.1 |
| Endosulfan sulfate | 0.614 | 0.032 | 2.0 |
| Imazalil | 0.678 | 0.042 | 2.1 |
| Pirimicarb | 0.676 | 0.040 | 2.0 |

The reference values for these Sample S1 analytes were in agreement with the robust averages of participants' results, within their respective associated uncertainties.

**Sample S2 Reference Values**

Sample S2 was analysed in two batches: a homogeneity batch and a transportation stability (refrigerated) batch. The homogeneity batch was quantitated by both primary LC-MS and confirmatory GC-MS methods. Reference values were obtained by averaging batch results.

The reference values obtained for the Sample S2 analytes are presented in Table 32.

Table 32 Reference Values for Sample S2 Lettuce

| Analyte | Reference Value (mg/kg) | Expanded Uncertainty (95%) (mg/kg) | Coverage Factor, k (95%) |
|---|---|---|---|
| Endosulfan sulfate | 0.750 | 0.109 | 2.2 |
| Pirimicarb | 0.702 | 0.039 | 2.2 |

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

### A2.2 Homogeneity Assessment

The process used to prepare the test samples has been demonstrated in previous NMI PT studies of similar analytes and matrices to produce sufficiently homogeneous samples. Furthermore, homogeneity testing was conducted for Samples S1, S2 and S3 in this study.

**Sample S1 Homogeneity Testing**

In addition to the Sample S1 analytes where reference values were obtained, homogeneity testing was also done for imidacloprid. This analysis was conducted as described above in Section A2.1 Reference Values, except using reference to D4-endosulfan sulfate instead of the deuterium-labelled analogue of imidacloprid.

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 33 to 39. Samples were found to be sufficiently homogeneous for use in a PT study with a target SD (as PCV) of 15%.

Table 33 Homogeneity Testing for Sample S1 Bifenthrin

| Bottle Number | S1 Bifenthrin (mg/kg) | |
|---|---|---|
| | Replicate 1 | Replicate 2 |
| 18 | 0.291 | 0.298 |
| 51 | 0.298 | 0.300 |
| 75 | 0.304 | 0.300 |
| 78 | 0.300 | 0.294 |
| 131 | 0.293 | 0.291 |
| 190 | 0.298 | 0.301 |
| 195 | 0.293 | 0.298 |
| 207 | 0.290 | 0.290 |
| 274 | 0.286 | 0.291 |
| 302 | 0.293 | 0.295 |
| Average | 0.295 | |
| CV | 1.6% | |

Thompson and Fearn Homogeneity Tests[16]

| Test | Value | Critical | Result |
|---|---|---|---|
| Cochran | 0.326 | 0.602 | **Pass** |
| $s_{an}/\sigma$ | 0.064 | 0.500 | **Pass** |
| $s^2_{sam}$ | 0.00001 | 0.00034 | **Pass** |

Table 34 Homogeneity Testing for Sample S1 Buprofezin

| Bottle Number | S1 Buprofezin (mg/kg) | |
|---|---|---|
| | Replicate 1 | Replicate 2 |
| 18 | 0.182 | 0.180 |
| 51 | 0.178 | 0.182 |
| 75 | 0.189 | 0.184 |
| 78 | 0.186 | 0.186 |
| 131 | 0.185 | 0.187 |
| 190 | 0.184 | 0.181 |
| 195 | 0.178 | 0.179 |
| 207 | 0.183 | 0.179 |
| 274 | 0.178 | 0.176 |
| 302 | 0.190 | 0.179 |
| Average | 0.182 | |
| CV | 2.1% | |

Thompson and Fearn Homogeneity Tests[16]

| Test | Value | Critical | Result |
|---|---|---|---|
| Cochran | 0.596 | 0.602 | **Pass** |
| $s_{an}/\sigma$ | 0.113 | 0.500 | **Pass** |
| $s^2_{sam}$ | 0.00001 | 0.00014 | **Pass** |

Table 35 Homogeneity Testing for Sample S1 Chlorpyrifos

| Bottle Number | S1 Chlorpyrifos (mg/kg) | |
|---|---|---|
| | Replicate 1 | Replicate 2 |
| 18 | 0.779 | 0.776 |
| 51 | 0.777 | 0.785 |
| 75 | 0.786 | 0.790 |
| 78 | 0.788 | 0.782 |
| 131 | 0.788 | 0.777 |
| 190 | 0.786 | 0.799 |
| 195 | 0.790 | 0.792 |
| 207 | 0.784 | 0.788 |
| 274 | 0.761 | 0.780 |
| 302 | 0.789 | 0.783 |
| Average | 0.784 | |
| CV | 1.0% | |

Thompson and Fearn Homogeneity Tests[16]

| Test | Value | Critical | Result |
|---|---|---|---|
| Cochran | 0.412 | 0.602 | **Pass** |
| $s_{an}/\sigma$ | 0.053 | 0.500 | **Pass** |
| $s^2_{sam}$ | 0.00002 | 0.00238 | **Pass** |

Table 36 Homogeneity Testing for Sample S1 Endosulfan Sulfate

| Bottle Number | S1 Endosulfan sulfate (mg/kg) | |
|---|---|---|
| | Replicate 1 | Replicate 2 |
| 18 | 0.609 | 0.615 |
| 51 | 0.615 | 0.628 |
| 75 | 0.627 | 0.603 |
| 78 | 0.621 | 0.618 |
| 131 | 0.613 | 0.617 |
| 190 | 0.608 | 0.620 |
| 195 | 0.619 | 0.615 |
| 207 | 0.622 | 0.616 |
| 274 | 0.598 | 0.604 |
| 302 | 0.627 | 0.617 |
| Average | 0.616 | |
| CV | 1.3% | |

Thompson and Fearn Homogeneity Tests[16]

| Test | Value | Critical | Result |
|---|---|---|---|
| Cochran | 0.523 | 0.602 | **Pass** |
| $s_{an}/\sigma$ | 0.081 | 0.500 | **Pass** |
| $s^2_{sam}$ | 0.00001 | 0.00150 | **Pass** |

Table 37 Homogeneity Testing for Sample S1 Imazalil

| Bottle Number | S1 Imazalil (mg/kg) | |
|---|---|---|
| | Replicate 1 | Replicate 2 |
| 18 | 0.666 | 0.684 |
| 51 | 0.674 | 0.683 |
| 75 | 0.674 | 0.683 |
| 78 | 0.693 | 0.684 |
| 131 | 0.685 | 0.690 |
| 190 | 0.681 | 0.689 |
| 195 | 0.690 | 0.684 |
| 207 | 0.684 | 0.686 |
| 274 | 0.683 | 0.686 |
| 302 | 0.688 | 0.688 |
| Average | 0.684 | |
| CV | 0.92% | |

Thompson and Fearn Homogeneity Tests[16]

| Test | Value | Critical | Result |
|---|---|---|---|
| Cochran | 0.461 | 0.602 | **Pass** |
| $s_{an}/\sigma$ | 0.058 | 0.500 | **Pass** |
| $s^2_{sam}$ | 0.00000 | 0.00181 | **Pass** |

Table 38 Homogeneity Testing for Sample S1 Imidacloprid

| Bottle Number | S1 Imidacloprid (mg/kg) | |
|---|---|---|
| | Replicate 1 | Replicate 2 |
| 18 | 0.364 | 0.366 |
| 51 | 0.364 | 0.367 |
| 75 | 0.366 | 0.365 |
| 78 | 0.373 | 0.369 |
| 131 | 0.370 | 0.369 |
| 190 | 0.370 | 0.364 |
| 195 | 0.360 | 0.362 |
| 207 | 0.366 | 0.363 |
| 274 | 0.373 | 0.365 |
| 302 | 0.363 | 0.362 |
| Average | 0.366 | |
| CV | 0.97% | |

Thompson and Fearn Homogeneity Tests[16]

| Test | Value | Critical | Result |
|---|---|---|---|
| Cochran | 0.429 | 0.602 | **Pass** |
| $s_{an}/\sigma$ | 0.048 | 0.500 | **Pass** |
| $s^2_{sam}$ | 0.00001 | 0.00052 | **Pass** |

Table 39 Homogeneity Testing for Sample S1 Pirimicarb

| Bottle Number | S1 Pirimicarb (mg/kg) | |
|---|---|---|
| | Replicate 1 | Replicate 2 |
| 18 | 0.671 | 0.677 |
| 51 | 0.677 | 0.680 |
| 75 | 0.673 | 0.676 |
| 78 | 0.678 | 0.676 |
| 131 | 0.680 | 0.681 |
| 190 | 0.678 | 0.676 |
| 195 | 0.674 | 0.684 |
| 207* | 0.692 | 0.673 |
| 274 | 0.682 | 0.673 |
| 302 | 0.686 | 0.682 |
| Average | 0.678 | |
| CV | 0.75% | |

Thompson and Fearn Homogeneity Tests[16]

| Test | Value | Critical | Result |
|---|---|---|---|
| Cochran | 0.377 | 0.639 | **Pass** |
| $s_{an}/\sigma$ | 0.036 | 0.500 | **Pass** |
| $s^2_{sam}$ | 0.00000 | 0.00182 | **Pass** |

* Results on bottle 207 were not included in the test for homogeneity, being identified as Cochran outliers due to the difference between replicates.[16]

**Sample S2 Homogeneity Testing**

For Sample S2 endosulfan sulfate and pirimicarb, homogeneity checks were performed as described above,[4,16] and these are presented in Tables 40 and 41. Samples were found to be sufficiently homogeneous for use in a PT study with a target SD (as PCV) of 15%.

Table 40 Homogeneity Testing for Sample S2 Endosulfan Sulfate

| Bottle Number | S2 Endosulfan sulfate (mg/kg) | |
|---|---|---|
| | Replicate 1 | Replicate 2 |
| 5 | 0.712 | 0.673 |
| 9 | 0.744 | 0.727 |
| 12 | 0.765 | 0.755 |
| 22 | 0.704 | 0.735 |
| 28 | 0.775 | 0.751 |
| 33 | 0.705 | 0.784 |
| 41 | 0.721 | 0.620 |
| 43 | 0.732 | 0.748 |
| 50 | 0.735 | 0.690 |
| 56 | 0.705 | 0.680 |
| Average | 0.723 | |
| CV | 5.4% | |

Thompson and Fearn Homogeneity Tests[16]

| Test | Value | Critical | Result |
|---|---|---|---|
| Cochran | 0.446 | 0.602 | **Pass** |
| $s_{an}/\sigma$ | 0.311 | 0.500 | **Pass** |
| $s^2_{sam}$ | 0.00040 | 0.00314 | **Pass** |

Table 41 Homogeneity Testing for Sample S2 Pirimicarb

| Bottle Number | S2 Pirimicarb (mg/kg) | |
|---|---|---|
| | Replicate 1 | Replicate 2 |
| 5 | 0.694 | 0.708 |
| 9 | 0.684 | 0.707 |
| 12 | 0.691 | 0.697 |
| 22 | 0.698 | 0.710 |
| 28 | 0.700 | 0.713 |
| 33 | 0.693 | 0.710 |
| 41 | 0.677 | 0.685 |
| 43 | 0.692 | 0.699 |
| 50 | 0.702 | 0.665 |
| 56 | 0.689 | 0.653 |
| Average | 0.693 | |
| CV | 2.2% | |

Thompson and Fearn Homogeneity Tests[16]

| Test | Value | Critical | Result |
|---|---|---|---|
| Cochran | 0.327 | 0.602 | **Pass** |
| $s_{an}/\sigma$ | 0.139 | 0.500 | **Pass** |
| $s^2_{sam}$ | 0.00002 | 0.00204 | **Pass** |

**Sample S3 Homogeneity Testing**

Homogeneity testing was done for Sample S3 chlorpyrifos and imidacloprid by NMI Port Melbourne (Food and Health Chemistry Laboratory).

Samples were analysed in duplicate and under repeatability conditions. The samples were prepared by accurately weighing 5 g of the sample then mixing with water to make a 10 mL solution. Methanol (20 mL) was then added and the solution was shaken and centrifuged.

For imidacloprid analysis, a 5 mL aliquot of the methanol solution was taken and mixed with 2 mL of a 20 g / 100 mL NaCl in $H_2O$ solution. A 5 mL aliquot of the salted solution was then transferred to a Chem-Elute column (5 mL) and eluted with 20 mL of dichloromethane. The eluate was evaporated to dryness and the residue dissolved in methanol/Milli-Q water (50:50). The resulting methanol solution was 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 MSMS Detector. Separation was performed on a Waters Acquity UPLC BEH C18 1.7 µm analytical LC column.

For chlorpyrifos analysis, once the 5 mL aliquot was taken out of the methanol solution as described above, 5 mL of acetone was added to the remaining solution and mixed. A 5 mL aliquot was then drawn from this solution and extracted in the same way as described above. 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 42 and 43. Samples were found to be sufficiently homogeneous for use in a PT study with a target SD (as PCV) of 20%.

Table 42 Homogeneity Testing for Sample S3 Chlorpyrifos

| Bottle Number | S3 Chlorpyrifos (mg/kg) | |
|---|---|---|
| | Replicate 1 | Replicate 2 |
| 4 | 0.14 | 0.12 |
| 11 | 0.13 | 0.13 |
| 21 | 0.12 | 0.11 |
| 22 | 0.16 | 0.14 |
| 25 | 0.15 | 0.15 |
| 32 | 0.10 | 0.12 |
| 35 | 0.12 | 0.15 |
| Average | 0.13 | |
| CV | 14% | |

Thompson and Fearn Homogeneity Tests[16]

| Test | Value | Critical | Result |
|---|---|---|---|
| Cochran | 0.386 | 0.727 | **Pass** |
| $s_{an}/\sigma$ | 0.491 | 0.500 | **Pass** |
| $s^2_{sam}$ | 0.00017 | 0.00037 | **Pass** |

Table 43 Homogeneity Testing for Sample S3 Imidacloprid

| Bottle Number | S3 Imidacloprid (mg/kg) | |
|---|---|---|
| | Replicate 1 | Replicate 2 |
| 4 | 0.061 | 0.055 |
| 11 | 0.059 | 0.055 |
| 21 | 0.055 | 0.056 |
| 22 | 0.055 | 0.061 |
| 25 | 0.058 | 0.053 |
| 32 | 0.056 | 0.051 |
| 35 | 0.052 | 0.058 |
| Average | 0.056 | |
| CV | 5.5% | |

Thompson and Fearn Homogeneity Tests[16]

| Test | Value | Critical | Result |
|---|---|---|---|
| Cochran | 0.242 | 0.727 | **Pass** |
| $s_{an}/\sigma$ | 0.316 | 0.500 | **Pass** |
| $s^2_{sam}$ | 0.00000 | 0.00004 | **Pass** |

**Participants' Results and Bottle Numbers**

Participants' results in this study also gave no reason to question the samples' homogeneity for the majority of analytes. Comparisons of *z* scores obtained to bottle number analysed by participants for all scored analytes are presented in Figures 59 to 73 (results have only been included when the participant was sent one sample set).

For Sample S3 linuron, due to the smaller number of participants reporting numeric results and the distribution of bottles that occurred, participants' results appear to show a fill order trend. NMI conducted additional testing for this analyte, and there was no evidence of any fill order trend.

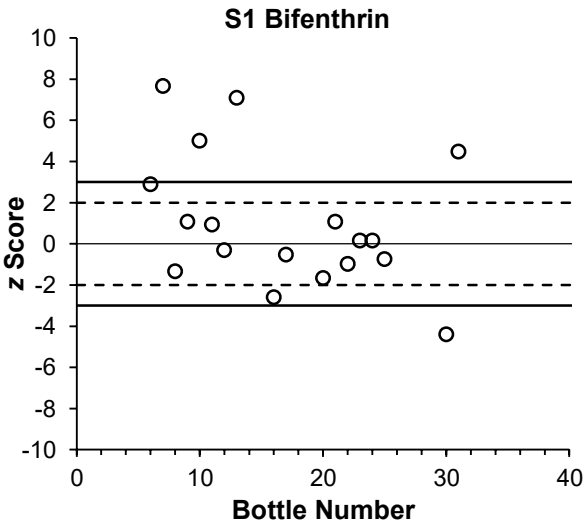


Figure 59 S1 Bifenthrin *z* Score vs Bottle Number

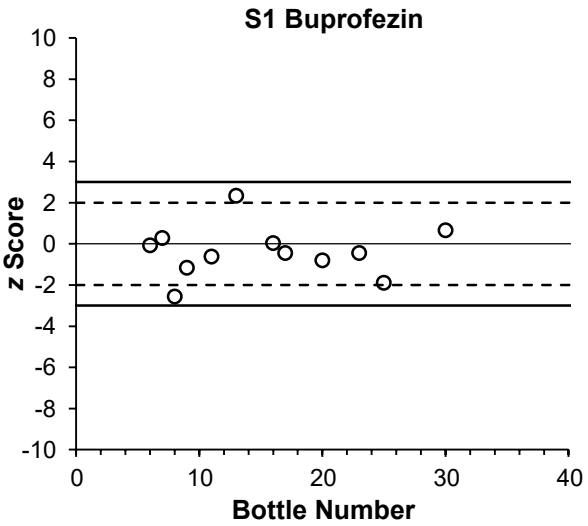


Figure 60 S1 Buprofezin *z* Score vs Bottle Number

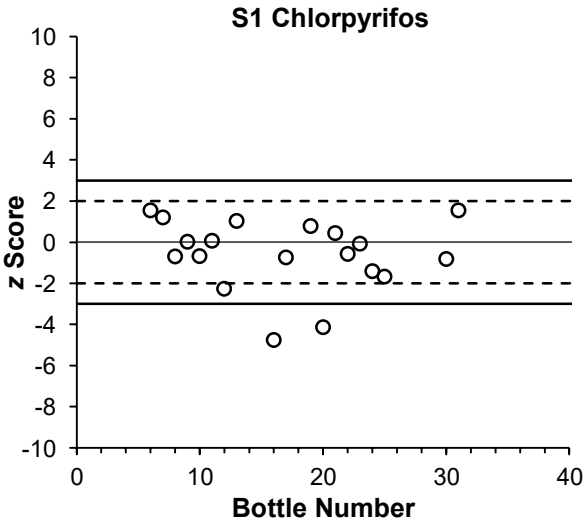


Figure 61 S1 Chlorpyrifos *z* Score vs Bottle Number

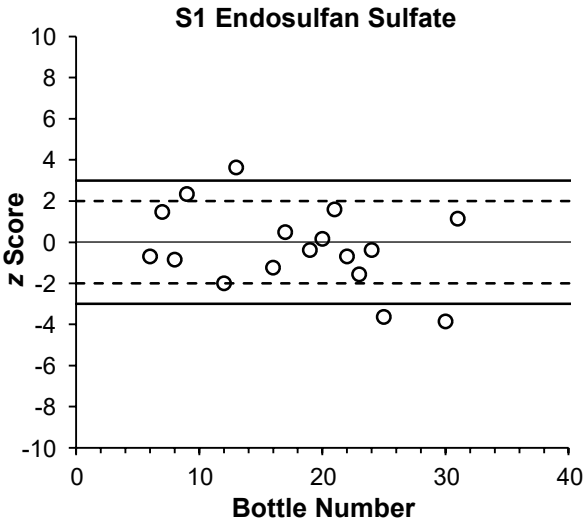


Figure 62 S1 Endosulfan Sulfate *z* Score vs Bottle Number

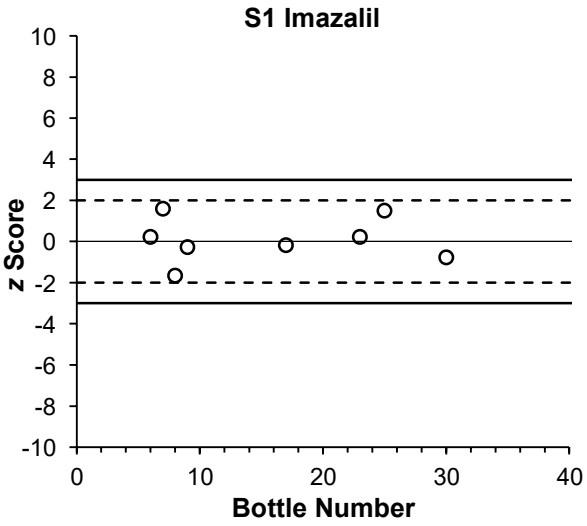


Figure 63 S1 Imazalil *z* Score vs Bottle Number

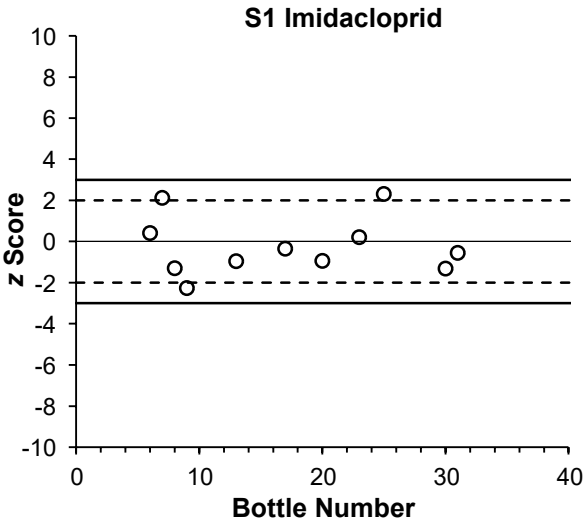


Figure 64 S1 Imidacloprid *z* Score vs Bottle Number

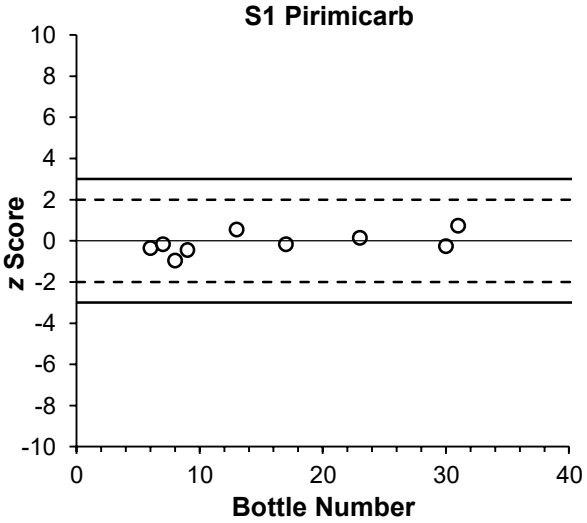


Figure 65 S1 Pirimicarb *z* Score vs Bottle Number

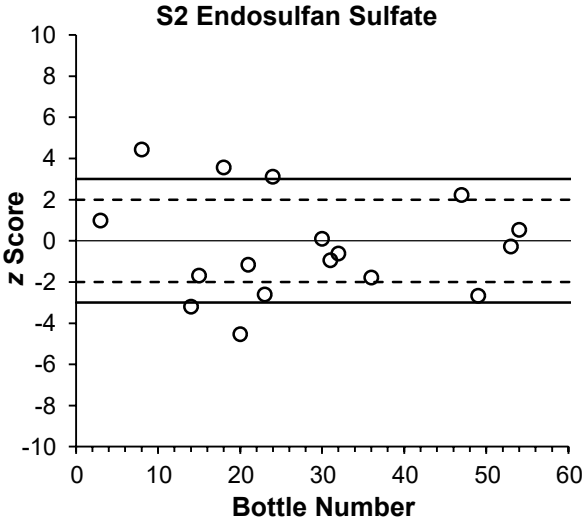


Figure 66 S2 Endosulfan Sulfate *z* Score vs Bottle Number

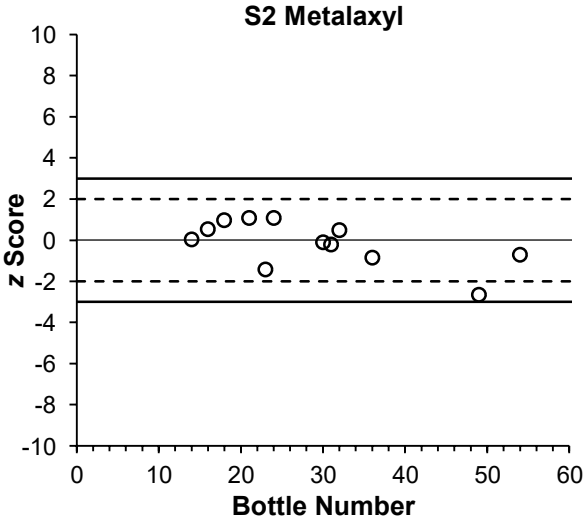


Figure 67 S2 Metalaxyl *z* Score vs Bottle Number

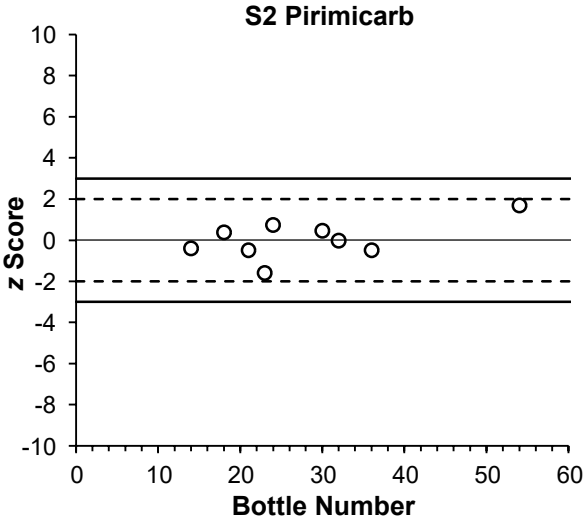


Figure 68 S2 Pirimicarb *z* Score vs Bottle Number

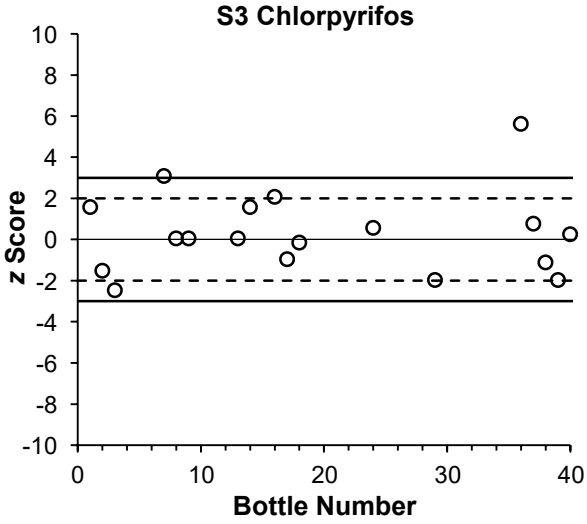


Figure 69 S3 Chlorpyrifos *z* Score vs Bottle Number

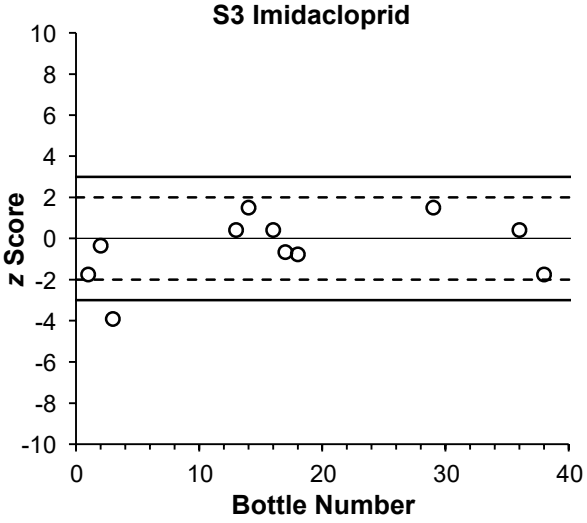


Figure 70 S3 Imidacloprid *z* Score vs Bottle Number

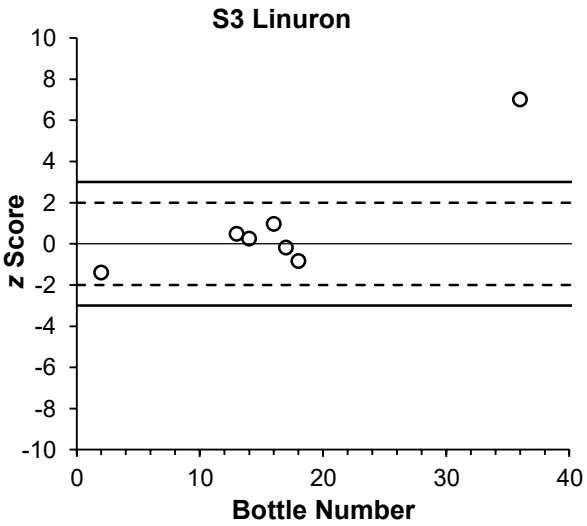


Figure 71 S3 Linuron *z* Score vs Bottle Number

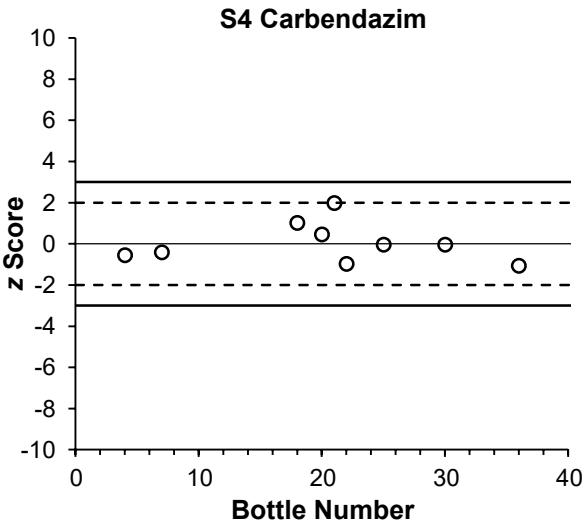


Figure 72 S4 Carbendazim *z* Score vs Bottle Number

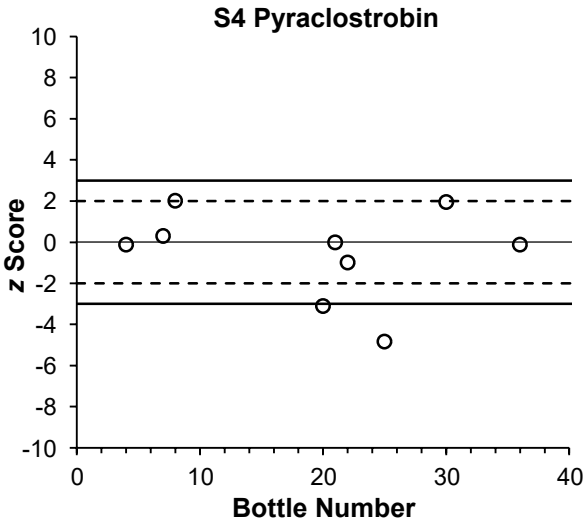


Figure 73 S4 Pyraclostrobin *z* Score vs Bottle Number

### A2.3 Stability Assessment

The process used to prepare, store and dispatch the test samples has been demonstrated in previous NMI PT studies of similar analytes and matrices to produce sufficiently stable samples. Furthermore, transportation stability testing was conducted for Samples S1 and S2 in this study.

The stability was assessed by transferring bottles to a refrigerator, to store at 4 °C, and/or to a cupboard, to store at room temperature (RT). A bottle was then returned to the freezer (-20 °C) after 14 days, and on completion of the stability study all samples were analysed in conjunction with reference bottles that had remained in the freezer.

**Sample S1 Stability Testing**

Stability testing was performed for all Sample S1 analytes, at both 4 °C and at RT.

Results were in agreement with each other and the assigned value within their respective uncertainties. Figures 74 to 80 present the spiked value, the stability testing results, and the final assigned value for each analyte. The samples were shown to be adequately stable when assessed against the criteria specified in ISO 13528:2022.[7]

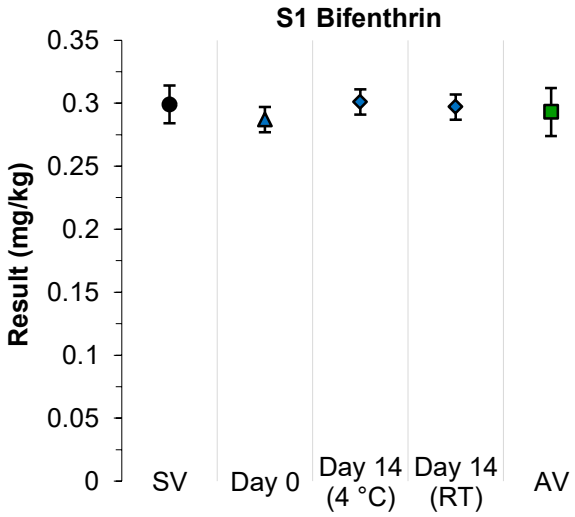


Figure 74 S1 Bifenthrin Stability Results

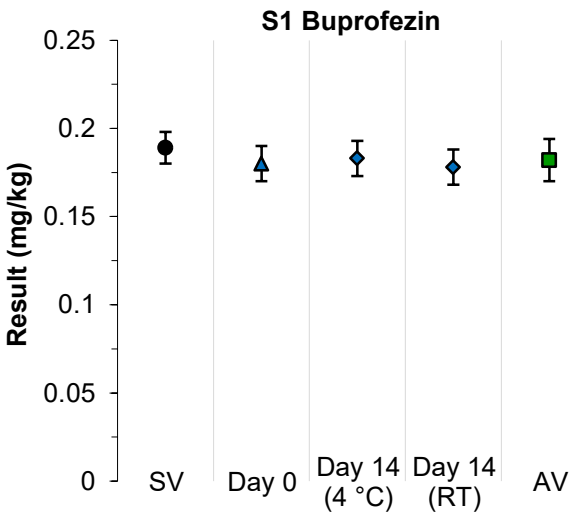


Figure 75 S1 Buprofezin Stability Results

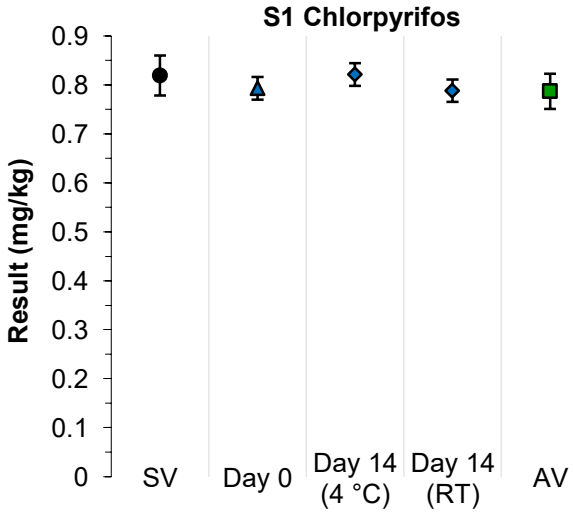


Figure 76 S1 Chlorpyrifos Stability Results

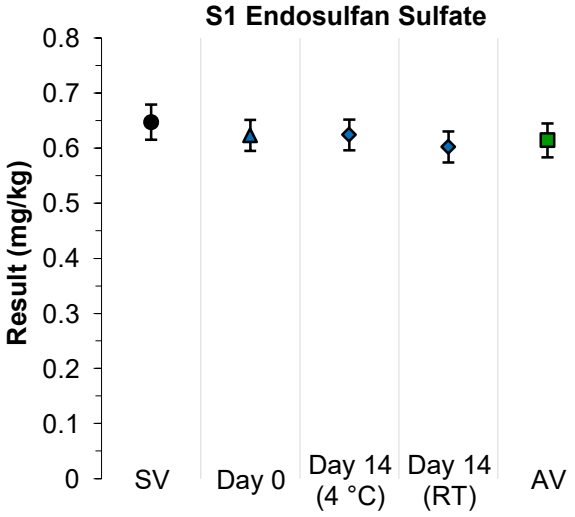


Figure 77 S1 Endosulfan Sulfate Stability Results

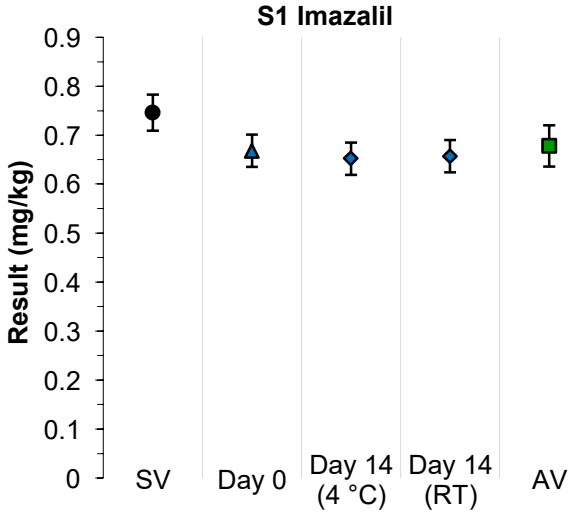


Figure 78 S1 Imazalil Stability Results

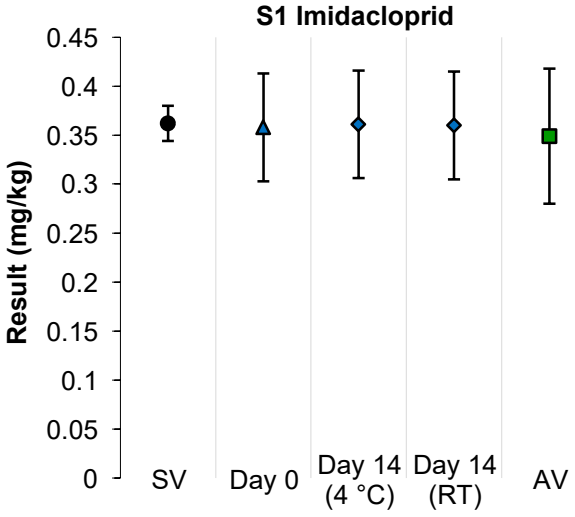


Figure 79 S1 Imidacloprid Stability Results

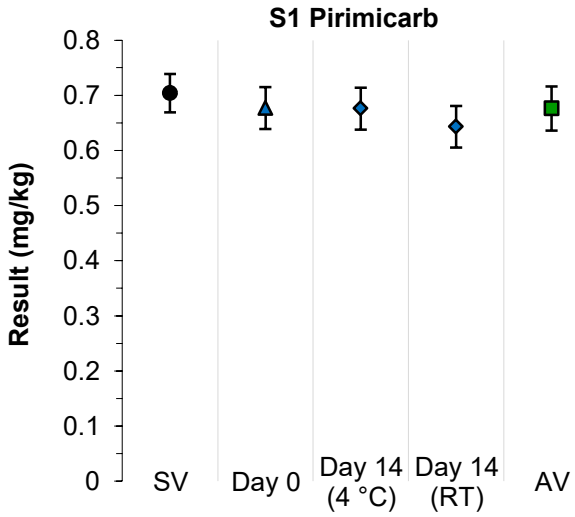


Figure 80 S1 Pirimicarb Stability Results

**Sample S2 Stability Testing**

Stability testing was performed for Sample S2 endosulfan sulfate and pirimicarb, at 4 °C.

Results were in agreement with each other and the assigned value within their respective uncertainties. Figures 81 and 82 present the spiked value, the stability testing results, and the final assigned value for each analyte. The samples were shown to be adequately stable when assessed against the criteria specified in ISO 13528:2022.[7]

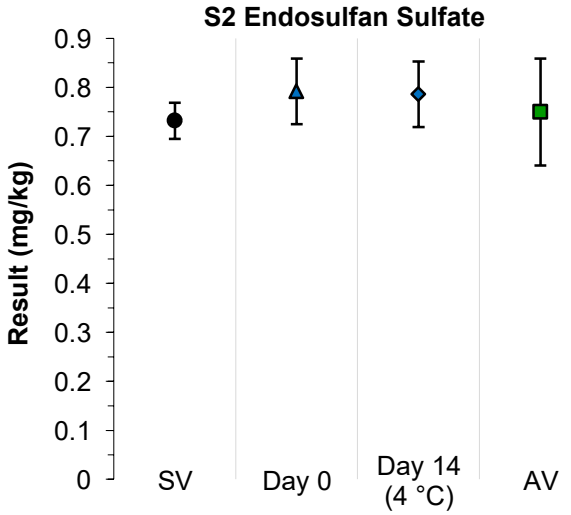


Figure 81 S2 Endosulfan Sulfate Stability Results

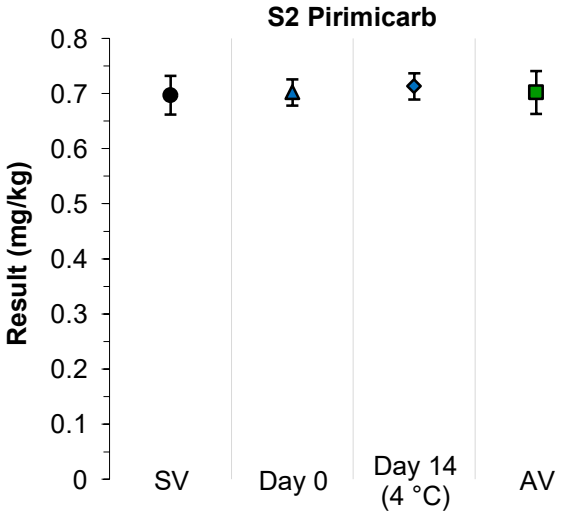


Figure 82 S2 Pirimicarb Stability Results

**Participants' Results and Days in Transit**

The samples were stored in a freezer at approximately -20 °C after preparation and prior to dispatch. The samples were then dispatched to participants in insulated polystyrene foam boxes with cooler bricks. Participants' results in this study gave no reason to question the samples' transportation stability. Comparisons of *z* scores obtained to days spent in transit for scored analytes are presented in Figures 83 to 97, and no evidence of analyte degradation with respect to the amount of time spent in transit was observed.

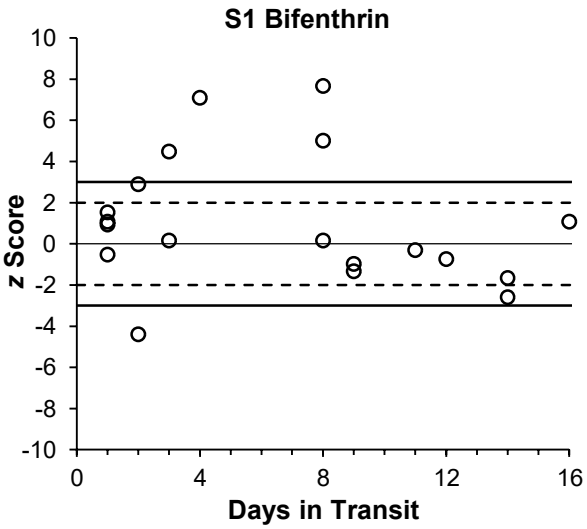


Figure 83 S1 Bifenthrin *z* Score vs Transit Days

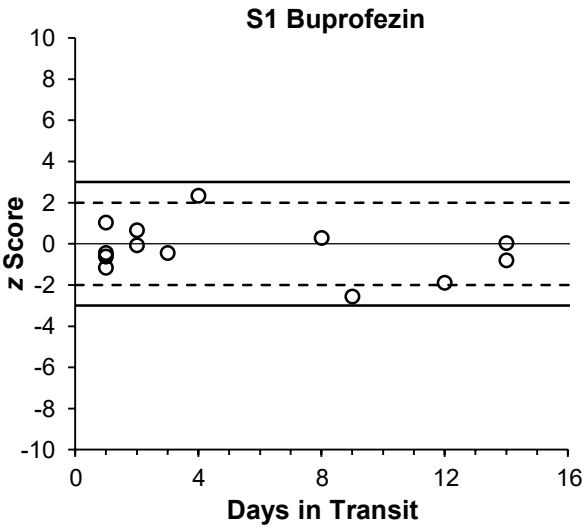


Figure 84 S1 Buprofezin *z* Score vs Transit Days

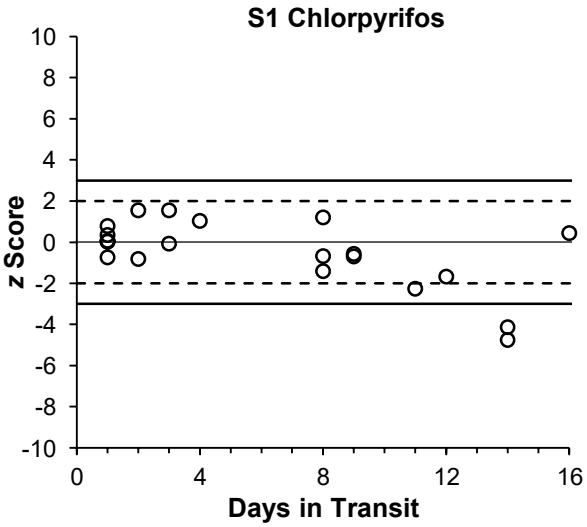


Figure 85 S1 Chlorpyrifos *z* Score vs Transit Days

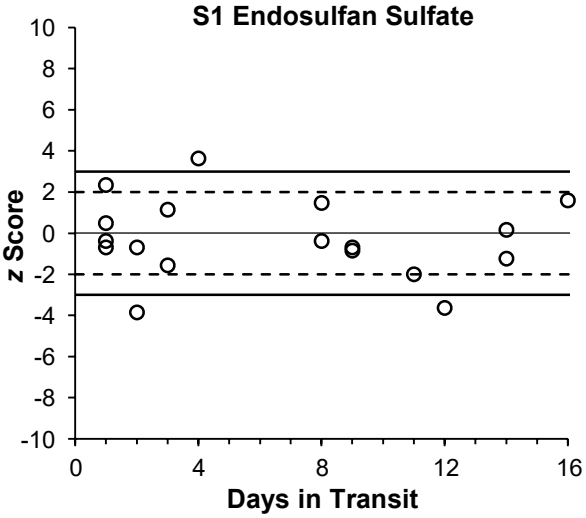


Figure 86 S1 Endosulfan Sulfate *z* Score vs Transit Days

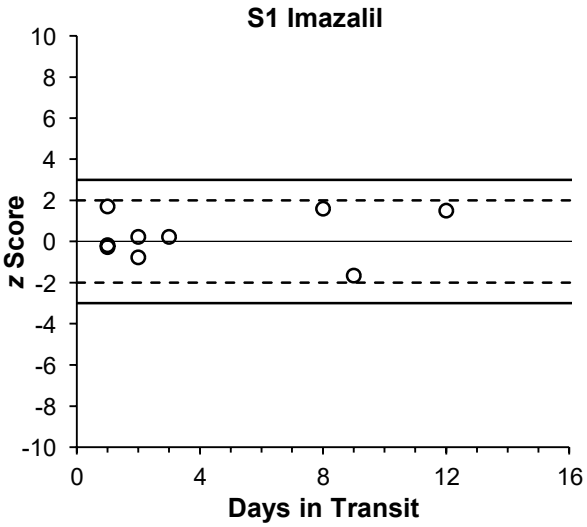


Figure 87 S1 Imazalil *z* Score vs Transit Days

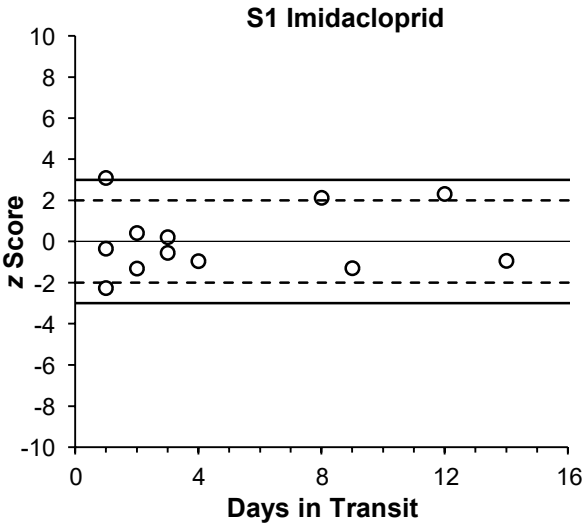


Figure 88 S1 Imidacloprid *z* Score vs Transit Days

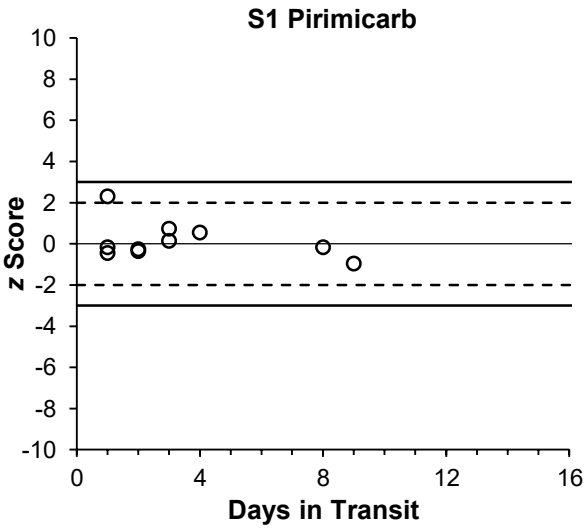


Figure 89 S1 Pirimicarb *z* Score vs Transit Days

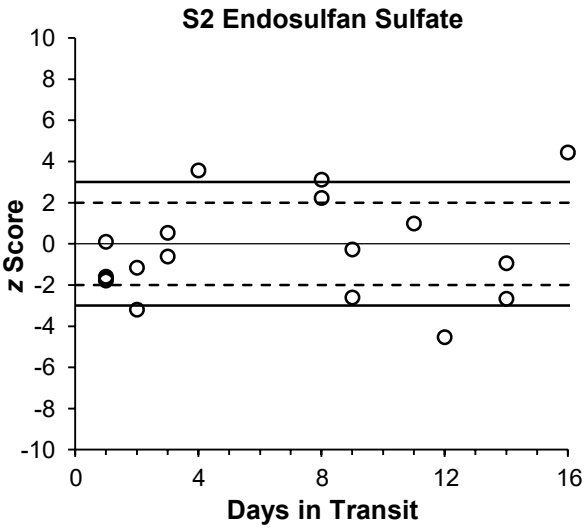


Figure 90 S2 Endosulfan Sulfate *z* Score vs Transit Days

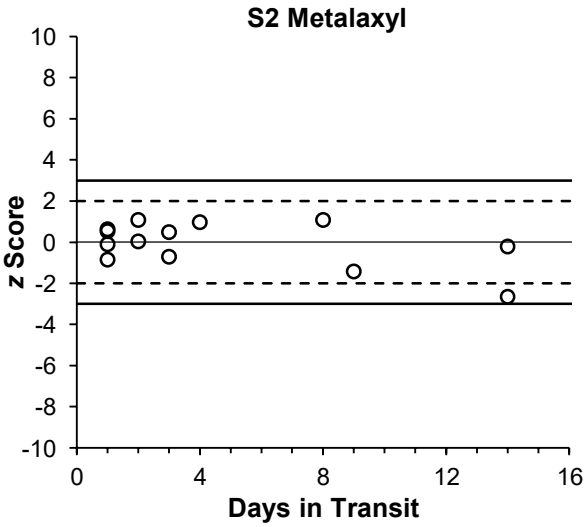


Figure 91 S2 Metalaxyl *z* Score vs Transit Days

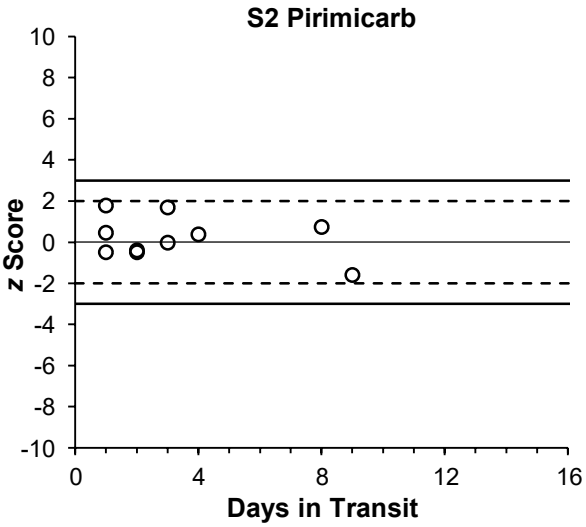


Figure 92 S2 Pirimicarb *z* Score vs Transit Days

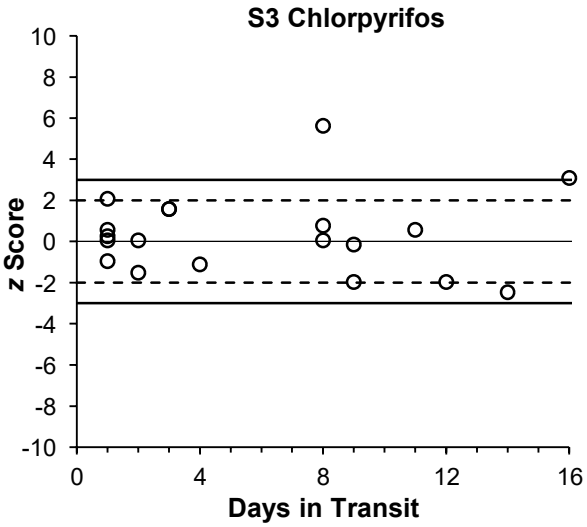


Figure 93 S3 Chlorpyrifos *z* Score vs Transit Days

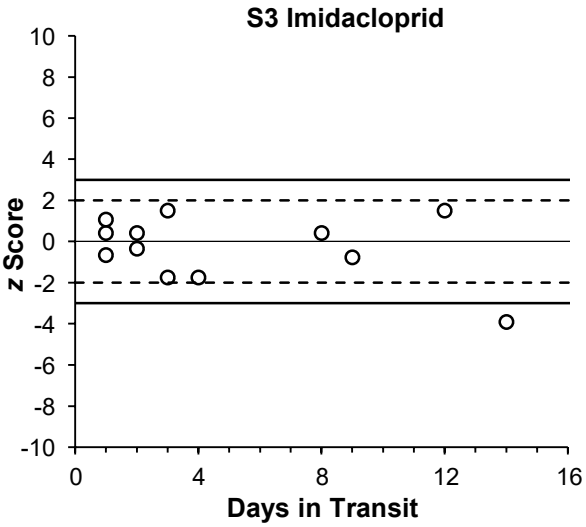


Figure 94 S3 Imidacloprid *z* Score vs Transit Days

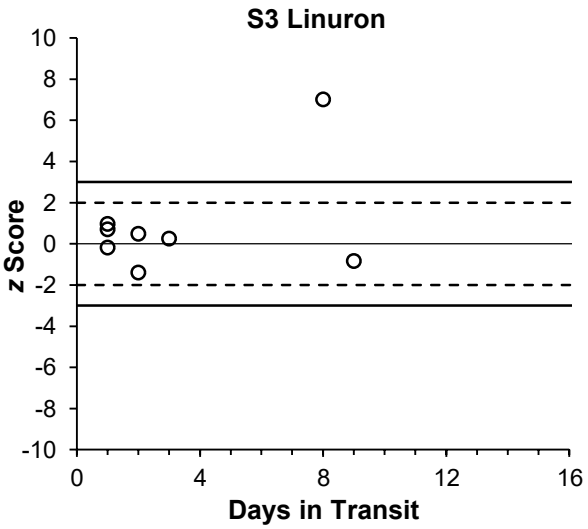


Figure 95 S3 Linuron *z* Score vs Transit Days

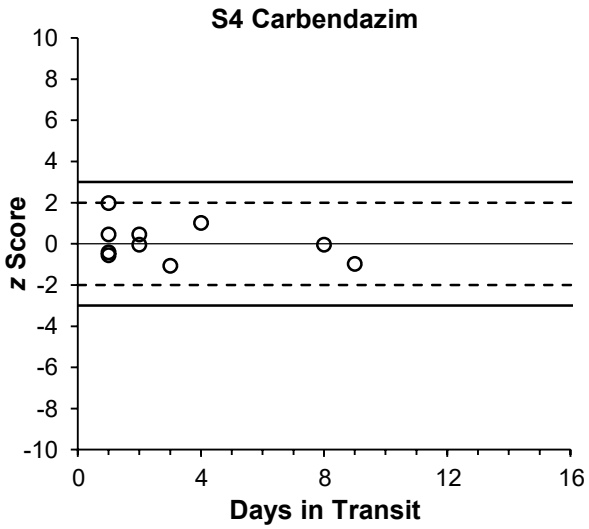


Figure 96 S4 Carbendazim *z* Score vs Transit Days

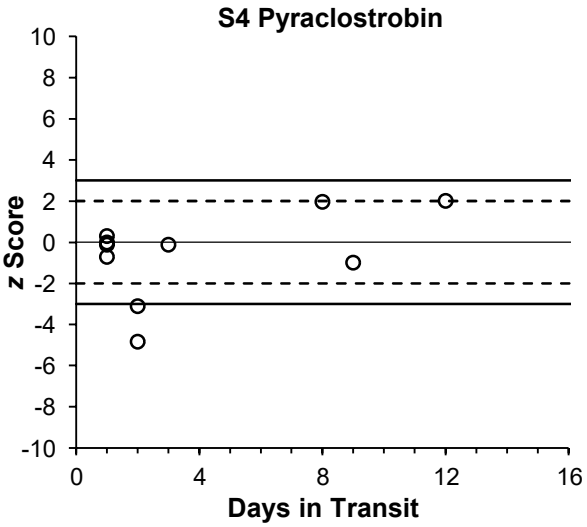


Figure 97 S4 Pyraclostrobin *z* Score vs Transit Days

## 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 13528:2022.[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 S2 metalaxyl is set out below in Table 44.

Table 44 Uncertainty of Robust Average for Sample S2 Metalaxyl

| | |
|---|---|
| Number of results ($p$) | 13 |
| Robust Average | 0.447 mg/kg |
| $S_{rob\ av}$ | 0.069 mg/kg |
| $u_{rob\ av}$ | 0.024 mg/kg |
| $k$ | 2 |
| $U_{rob\ av}$ | 0.048 mg/kg |

Therefore, the robust average for Sample S2 metalaxyl in Sample S1 is 0.447 ± 0.048 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 (Sections 4.7 and 4.8).

A worked example for the result reported by Laboratory 1 for Sample S3 chlorpyrifos is set out below in Table 45.

Table 45 $z$ Score and $E_n$ Score for Sample S3 Chlorpyrifos Result Reported by Laboratory 1

| Participant Result (mg/kg) | Assigned Value (mg/kg) | Target Standard Deviation | $z$ Score | $E_n$ Score |
|---|---|---|---|---|
| 0.11 ± 0.033 | 0.099 ± 0.0017 | 20% as CV, or: 0.2 × 0.099 = 0.0198 mg/kg | $z = \frac{0.11 - 0.099}{0.0198} = 0.56$ | $E_n = \frac{0.11 - 0.099}{\sqrt{0.033^2 + 0.017^2}} = 0.30$ |

## APPENDIX 4 PARTICIPANTS' TEST METHODS

Participants were requested to provide information about their test methods. Responses are presented in Tables 46 to 63. Some responses may be modified so that the participant cannot be identified.

Table 46 Analysis of Blank Sample and Sample Mass Used

| Lab. Code | Blank Analysed? | S1 Sample Mass (g) | S2 Sample Mass (g) | S3 Sample Mass (g) | S4 Sample Mass (g) |
|---|---|---|---|---|---|
| 1 | Yes | | | | |
| 2 | Yes | 10 | 10 | 10 | 10 |
| 3 | Yes | 20 | 20 | 20 | 20 |
| 4 | Yes | 15 | 15 | 15 | 15 |
| 5 | Yes | 10 | 10 | 10 | 10 |
| 6 | Yes | | | | |
| 7 | Yes | 10 | 10 | 10 | 10 |
| 8 | Yes | 10 | 10 | 10 | 10 |
| 9 | No | 10 | 10 | 5 | 10 |
| 10 | Yes | 15 | 15 | 15 | 15 |
| 11 | Yes | 15 | 15 | 15 | 15 |
| 12 | No | 20 | 20 | 20 | 20 |
| 13 | Yes | 20 | 20 | 20 | 20 |
| 14 | Yes | 20 | 20 | 20 | 20 |
| 15 | Yes | 10 | 10 | 10 | 10 |
| 16 | Yes | 10 | 10 | 10 | 10 |
| 17 | Yes | 10 | 10 | 10 | 10 |
| 18 | Yes | 10 | 10 | 10 | 10 |
| 19 | Yes | 10 | 10 | 10 | 10 |
| 20 | No | 20 and 10 | 20 and 10 | 20 and 10 | 20 and 10 |

Table 47 Sample S1 Tomato Bifenthrin Methodology

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument | Comments |
|---|---|---|---|---|---|
| 1 | | | | | |
| 2 | QuEChERS | Acetonitrile | | LC-MS/MS | |
| 3 | QuEChERS | Hexane | deactivate silica gel | GC-ECD | |
| 4 | QuEChERS | Acetonitrile | SPE | GC-MS | |
| 5 | QuEChERS | 1%Acetic acid/Acetonitrile | Dispersive SPE | GC-MS | |
| 6 | NT | | | | |
| 7 | QuEChERS | Acetonitrile | PSA | LC-MS/MS | |
| 8 | QuEChERS | Acetonitrile | Dispersive SPE | GC-MS/MS | |
| 9 | QuEChERS | Acetonitrile | PSA | GC-MS/MS | |
| 10 | QuEChERS | ACN | PSA | GC-MS/MS | |
| 11 | QuEChERS | Acetonitrile (1% acetic acid) | C18 / PSA | GC-MS/MS | |
| 12 | QuEChERS | Acetonitrile | dispersive-SPE | GC-ECD | |
| 13 | QuEChERS | Acetonitrile | Florisil | GC-ECD | |
| 14 | Solid-Liquid | DCM,Hex,Acetone | | GC-MS/MS | |
| 15 | QuEChERS | Acetonitrile | 150 mg PSA, 900 mg MgSO4 | GC-ECD | Confirmatory analysis using GC-MS |
| 16 | SPE | Acetonitrile | GCE-C18-Florisil | GC-MS | |
| 17 | SPE | acetonitrile | C18,envicarb,florisil | GC-ECD | |
| 18 | SPE | Acetonitrile | C18, carbon, florisil | GC-ECD | |
| 19 | QuEChERS | ACN | d-SPE | GC-MS/MS | |
| 20 | QuEChERS | acetonitrile | Dispersive Solid Phase Extraction (d-spe) | LC-MSMS | |

Table 48 Sample S1 Tomato Buprofezin Methodology

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|
| 1 | | | | |
| 2 | QuEChERS | Acetonitrile | | LC-MS/MS |
| 3 | NT | | | |
| 4 | QuEChERS | Acetonitrile | SPE | GC-MS |
| 5 | NT | | | |
| 6 | NT | | | |
| 7 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 8 | QuEChERS | Acetonitrile | Dispersive SPE | LC-MS/MS |
| 9 | QuEChERS | Acetonitrile | PSA | GC-MS/MS |
| 10 | QuEChERS | ACN | PSA | LC-MS/MS |
| 11 | QuEChERS | Acetonitrile (1% acetic acid) | C18 / PSA | LC-MS/MS |
| 12 | NT | | | |
| 13 | | | | |
| 14 | Solid-Liquid | DCM,Hex,Acetone | | GCMSMS &LCMSMS |
| 15 | NT | | | |
| 16 | SPE | Acetonitrile | GCE-C18-Florisil | GC-MS |
| 17 | SPE | acetonitrile | C18,envicarb,florisil | LCMS/MS |
| 18 | NT | | | |
| 19 | QuEChERS | ACN | d-SPE | LC-MS/MS |
| 20 | QuEChERS | acetonitrile | Dispersive Solid Phase Extraction (d-spe) | LC-MSMS |

Table 49 Sample S1 Tomato Chlorpyrifos Methodology

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument | Comments |
|---|---|---|---|---|---|
| 1 | | | | | |
| 2 | QuEChERS | Acetonitrile | PSA | GC-MS/MS | |
| 3 | Quechers | Acetonitrile | | GC-FPD | |
| 4 | QuEChERS | Acetonitrile | SPE | GC-MS | |
| 5 | QuEChERS | 1%Acetic acid/Acetonitrile | Dispersive SPE | GC-MS | |
| 6 | | | | | |
| 7 | QuEChERS | Acetonitrile | PSA | GC-MS/MS | |
| 8 | QuEChERS | Acetonitrile | Dispersive SPE | GC-MS/MS | |
| 9 | QuEChERS | Acetonitrile | PSA | GC-MS/MS | |
| 10 | QuEChERS | ACN | PSA | LC-MS/MS | |
| 11 | QuEChERS | Acetonitrile (1% acetic acid) | C18 / PSA | GC-MS/MS | |
| 12 | QuEChERS | Acetonitrile | dispersive-SPE | GC-FPD | |
| 13 | QuEChERS | Acetonitrile | Florisil | GC-FPD | |
| 14 | Solid-Liquid | DCM,Hex,Acetone | | GCMSMS &LCMSMS | |
| 15 | QuEChERS | Acetonitrile | 150 mg PSA, 900 mg MgSO4 | GC-FPD | Confirmatory analysis using GC-MS |
| 16 | SPE | Acetonitrile | GCE-C18-Florisil | GC-MS | |
| 17 | SPE | acetonitrile | C18,envicarb,florisil | GC-NPD | |
| 18 | SPE | Acetonitrile | C18, carbon, florisil | GC-NPD | |
| 19 | QuEChERS | ACN | d-SPE | GC-MS/MS | |
| 20 | QuEChERS | acetonitrile | Dispersive Solid Phase Extraction (d-spe) | GC-FPD | |

Table 50 Sample S1 Tomato Endosulfan Sulfate Methodology

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument | Comments |
|---|---|---|---|---|---|
| 1 | | | | | |
| 2 | QuEChERS | Acetonitrile | PSA | GC-MS/MS | |
| 3 | QuEChERS | Hexane | deactivate silica gel | GC-ECD | |
| 4 | QuEChERS | Acetonitrile | SPE | GC-MS | |
| 5 | QuEChERS | 1%Acetic acid/Acetonitrile | Dispersive SPE | GC-MS | |
| 6 | | | | | |
| 7 | QuEChERS | Acetonitrile | PSA | GC-MS/MS | |
| 8 | QuEChERS | Acetonitrile | Dispersive SPE | GC-MS/MS | |
| 9 | QuEChERS | Acetonitrile | PSA | GC-MS/MS | |
| 10 | NT | | | | |
| 11 | QuEChERS | Acetonitrile (1% acetic acid) | C18 / PSA | GC-MS/MS | |
| 12 | QuEChERS | Acetonitrile | dispersive-SPE | GC-ECD | |
| 13 | QuEChERS | Acetonitrile | Florisil | GC-ECD | |
| 14 | Solid-Liquid | DCM,Hex,Acetone | | GC-MS/MS | |
| 15 | QuEChERS | Acetonitrile | 152 mg PSA, 900 mg MgSO4 | GC-ECD | Confirmatory analysis using GC-MS |
| 16 | SPE | Acetonitrile | GCE-C18-Florisil | GC-MS | |
| 17 | SPE | acetonitrile | C18,envicarb,florisil | GC-ECD | |
| 18 | SPE | Acetonitrile | C18, carbon, florisil | GC-ECD | |
| 19 | QuEChERS | ACN | d-SPE | GC-MS/MS | |
| 20 | QuEChERS | acetonitrile | Dispersive Solid Phase Extraction (d-spe) | GC-MSMS | |

Table 51 Sample S1 Tomato Imazalil Methodology

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|
| 1 | | | | |
| 2 | QuEChERS | Acetonitrile | | LC-MS/MS |
| 3 | NT | | | |
| 4 | NT | | | |
| 5 | NT | | | |
| 6 | NT | | | |
| 7 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 8 | QuEChERS | Acetonitrile | Dispersive SPE | LC-MS/MS |
| 9 | QuEChERS | Acetonitrile | PSA | GC-MS/MS |
| 10 | NT | | | |
| 11 | QuEChERS | Acetonitrile (1% acetic acid) | C18 / PSA | LC-MS/MS |
| 12 | NT | | | |
| 13 | | | | |
| 14 | Solid-Liquid | DCM,Hex,Acetone | | GCMSMS &LCMSMS |
| 15 | NT | | | |
| 16 | QuEChERS | Acetonitrile | dSPE | LC-MS/MS |
| 17 | NT | | | |
| 18 | NT | | | |
| 19 | QuEChERS | ACN | d-SPE | LC-MS/MS |
| 20 | NT | | | |

Table 52 Sample S1 Tomato Imidacloprid Methodology

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|
| 1 | | | | |
| 2 | QuEChERS | Acetonitrile | | LC-MS/MS |
| 3 | NT | | | |
| 4 | NT | | | |
| 5 | QuEChERS | 1%Acetic acid/Acetonitrile | | LC-MS/MS |
| 6 | NT | | | |
| 7 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 8 | QuEChERS | Acetonitrile | Dispersive SPE | LC-MS/MS |
| 9 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 10 | NT | | | |
| 11 | QuEChERS | Acetonitrile (1% acetic acid) | C18 / PSA | LC-MS/MS |
| 12 | NT | | | |
| 13 | | | | |
| 14 | Solid-Liquid | DCM,Hex,Acetone | | LC-MS/MS |
| 15 | NT | | | |
| 16 | QuEChERS | Acetonitrile | dSPE | LC-MS/MS |
| 17 | SPE | acetonitrile | C18,envicarb,florisil | LCMS/MS |
| 18 | NT | | | |
| 19 | QuEChERS | ACN | d-SPE | LC-MS/MS |
| 20 | QuEChERS | acetonitrile | Dispersive Solid Phase Extraction (d-spe) | LC-MSMS |

Table 53 Sample S1 Tomato Pirimicarb Methodology

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|
| 1 | | | | |
| 2 | QuEChERS | Acetonitrile | | LC-MS/MS |
| 3 | NT | | | |
| 4 | NT | | | |
| 5 | QuEChERS | 1%Acetic acid/Acetonitrile | Dispersive SPE | GC-MS |
| 6 | NT | | | |
| 7 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 8 | QuEChERS | Acetonitrile | Dispersive SPE | LC-MS/MS |
| 9 | QuEChERS | Acetonitrile | PSA | GC-MS/MS |
| 10 | NT | | | |
| 11 | QuEChERS | Acetonitrile (1% acetic acid) | C18 / PSA | LC-MS/MS |
| 12 | NT | | | |
| 13 | | | | |
| 14 | Solid-Liquid | DCM,Hex,Acetone | | GCMSMS &LCMSMS |
| 15 | NT | | | |
| 16 | NT | | | |
| 17 | NT | | | |
| 18 | NT | | | |
| 19 | QuEChERS | ACN | d-SPE | LC-MS/MS |
| 20 | QuEChERS | acetonitrile | Dispersive Solid Phase Extraction (d-spe) | LC-MSMS |

Table 54 Sample S2 Lettuce Endosulfan Sulfate Methodology

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument | Comments |
|---|---|---|---|---|---|
| 1 | | | | | |
| 2 | QuEChERS | Acetonitrile | PSA | GC-MS/MS | |
| 3 | QuEChERS | Hexane | deactivate silica gel | GC-ECD | |
| 4 | QuEChERS | Acetonitrile | SPE | GC-MS | |
| 5 | QuEChERS | 1%Acetic acid/Acetonitrile | Dispersive SPE | GC-MS | |
| 6 | | | | | |
| 7 | QuEChERS | Acetonitrile | PSA | GC-MS/MS | |
| 8 | QuEChERS | Acetonitrile | Dispersive SPE | GC-MS/MS | |
| 9 | QuEChERS | Acetonitrile | PSA | GC-MS/MS | |
| 10 | NT | | | | |
| 11 | QuEChERS | Acetonitrile (1% acetic acid) | C18 / PSA | GC-MS/MS | |
| 12 | QuEChERS | Acetonitrile | dispersive-SPE | GC-ECD | |
| 13 | QuEChERS | Acetonitrile | Florisil | GC-ECD | |
| 14 | Solid-Liquid | DCM,Hex,Acetone | | GC-MS/MS | |
| 15 | QuEChERS | Acetonitrile | 154 mg PSA, 45 mg GCB, 855 mg MgSO4 | GC-ECD | Confirmatory analysis using GC-MS |
| 16 | SPE | Acetonitrile | GCE-C18-Florisil | GC-ECD | |
| 17 | SPE | acetonitrile | C18,envicarb,florisil | GC-ECD | |
| 18 | SPE | Acetonitrile | C18, carbon, florisil | GC-ECD | |
| 19 | QuEChERS | ACN | d-SPE | GC-MS/MS | |
| 20 | QuEChERS | acetonitrile | Dispersive Solid Phase Extraction (d-spe) | GC-MSMS | |

Table 55 Sample S2 Lettuce Metalaxyl Methodology

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|
| 1 | | | | |
| 2 | QuEChERS | Acetonitrile | | LC-MS/MS |
| 3 | NT | | | |
| 4 | QuEChERS | Acetonitrile | SPE | GC-MS |
| 5 | QuEChERS | 1%Acetic acid/Acetonitrile | Dispersive SPE | GC-MS |
| 6 | NT | | | |
| 7 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 8 | QuEChERS | Acetonitrile | Dispersive SPE | LC-MS/MS |
| 9 | QuEChERS | Acetonitrile | PSA | GC-MS/MS |
| 10 | QuEChERS | ACN | PSA | LC-MS/MS |
| 11 | QuEChERS | Acetonitrile (1% acetic acid) | C18 / PSA | LC-MS/MS |
| 12 | NT | | | |
| 13 | | | | |
| 14 | Solid-Liquid | DCM,Hex,Acetone | | GCMSMS &LCMSMS |
| 15 | NT | | | |
| 16 | NT | | | |
| 17 | SPE | acetonitrile | C18,envicarb,florisil | LCMS/MS |
| 18 | NT | | | |
| 19 | QuEChERS | ACN | d-SPE | LC-MS/MS |
| 20 | QuEChERS | acetonitrile | Dispersive Solid Phase Extraction (d-spe) | LC-MSMS |

Table 56 Sample S2 Lettuce Permethrin Methodology

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument | Comments |
|---|---|---|---|---|---|
| 1 | | | | | |
| 2 | QuEChERS | Acetonitrile | PSA | GC-MS/MS | |
| 3 | | | | | |
| 4 | QuEChERS | Acetonitrile | SPE | GC-MS | |
| 5 | QuEChERS | 1%Acetic acid/Acetonitrile | Dispersive SPE | GC-MS | |
| 6 | NT | | | | |
| 7 | QuEChERS | Acetonitrile | PSA | GC-MS/MS | |
| 8 | QuEChERS | Acetonitrile | Dispersive SPE | GC-MS/MS | |
| 9 | QuEChERS | Acetonitrile | PSA | GC-MS/MS | |
| 10 | NT | | | | |
| 11 | QuEChERS | Acetonitrile (1% acetic acid) | C18 / PSA | GC-MS/MS | |
| 12 | QuEChERS | Acetonitrile | dispersive-SPE | GC-ECD | |
| 13 | | | | | |
| 14 | Solid-Liquid | DCM,Hex,Acetone | | GC-MS/MS | |
| 15 | QuEChERS | Acetonitrile | 154 mg PSA, 45 mg GCB, 855 mg MgSO4 | GC-ECD | Confirmatory analysis using GC-MS |
| 16 | SPE | Acetonitrile | GCE-C18-Florisil | GC-ECD | |
| 17 | SPE | acetonitrile | C18,envicarb,florisil | GC-ECD | |
| 18 | SPE | Acetonitrile | C18, carbon, florisil | GC-ECD | |
| 19 | QuEChERS | ACN | d-SPE | GC-MS/MS | |
| 20 | | | | | |

Table 57 Sample S2 Lettuce Pirimicarb Methodology

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|
| 1 | | | | |
| 2 | QuEChERS | Acetonitrile | | LC-MS/MS |
| 3 | NT | | | |
| 4 | NT | | | |
| 5 | QuEChERS | 1%Acetic acid/Acetonitrile | Dispersive SPE | GC-MS |
| 6 | NT | | | |
| 7 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 8 | QuEChERS | Acetonitrile | Dispersive SPE | LC-MS/MS |
| 9 | QuEChERS | Acetonitrile | PSA | GC-MS/MS |
| 10 | NT | | | |
| 11 | QuEChERS | Acetonitrile (1% acetic acid) | C18 / PSA | LC-MS/MS |
| 12 | NT | | | |
| 13 | | | | |
| 14 | Solid-Liquid | DCM,Hex,Acetone | | GCMSMS &LCMSMS |
| 15 | NT | | | |
| 16 | NT | | | |
| 17 | NT | | | |
| 18 | NT | | | |
| 19 | QuEChERS | ACN | d-SPE | LC-MS/MS |
| 20 | QuEChERS | acetonitrile | Dispersive Solid Phase Extraction (d-spe) | LC-MSMS |

Table 58 Sample S3 Parsley Chlorpyrifos Methodology

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument | Comments |
|---|---|---|---|---|---|
| 1 | | | | | |
| 2 | QuEChERS | Acetonitrile | PSA | GC-MS/MS | |
| 3 | Quechers | Acetonitrile | | GC-FPD | |
| 4 | | | | | |
| 5 | QuEChERS | 1%Acetic acid/Acetonitrile | Dispersive SPE | GC-MS | |
| 6 | | | | | |
| 7 | QuEChERS | Acetonitrile | PSA | GC-MS/MS | |
| 8 | QuEChERS | Acetonitrile | Dispersive SPE | GC-MS/MS | |
| 9 | QuEChERS | Acetonitrile | PSA | GC-MS/MS | |
| 10 | QuEChERS | ACN | PSA | LC-MS/MS | |
| 11 | QuEChERS | Acetonitrile (1% acetic acid) | C18 / PSA | GC-MS/MS | |
| 12 | QuEChERS | Acetonitrile | dispersive-SPE | GC-FPD | |
| 13 | QuEChERS | Acetonitrile | Florisil | GC-FPD | |
| 14 | Solid-Liquid | DCM,Hex,Acetone | | GCMSMS &LCMSMS | |
| 15 | QuEChERS | Acetonitrile | 152 mg PSA, 45 mg GCB, 855 mg MgSO4 | GC-FPD | Confirmatory analysis using GC-MS |
| 16 | SPE | Acetonitrile | GCE-C18-florisil | GC-FPD | |
| 17 | SPE | acetonitrile | C18,envicarb,florisil | GC-NPD | |
| 18 | SPE | Acetonitrile | C18, carbon, florisil | GC-NPD | |
| 19 | QuEChERS | ACN | d-SPE | GC-MS/MS | |
| 20 | QuEChERS | acetonitrile | Dispersive Solid Phase Extraction (d-spe) | GC-FPD | |

Table 59 Sample S3 Parsley Imidacloprid Methodology

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|
| 1 | | | | |
| 2 | QuEChERS | Acetonitrile | | LC-MS/MS |
| 3 | NT | | | |
| 4 | NT | | | |
| 5 | QuEChERS | 1%Acetic acid/Acetonitrile | | LC-MS/MS |
| 6 | NT | | | |
| 7 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 8 | QuEChERS | Acetonitrile | Dispersive SPE | LC-MS/MS |
| 9 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 10 | NT | | | |
| 11 | QuEChERS | Acetonitrile (1% acetic acid) | C18 / PSA | LC-MS/MS |
| 12 | NT | | | |
| 13 | | | | |
| 14 | Solid-Liquid | DCM,Hex,Acetone | | LC-MS/MS |
| 15 | NT | | | |
| 16 | QuEChERS | Acetonitrile | dSPE | LC-MS/MS |
| 17 | SPE | acetonitrile | C18,envicarb,florisil | LCMS/MS |
| 18 | NT | | | |
| 19 | QuEChERS | ACN | d-SPE | LC-MS/MS |
| 20 | QuEChERS | acetonitrile | Dispersive Solid Phase Extraction (d-spe) | LC-MSMS |

Table 60 Sample S3 Parsley Linuron Methodology

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|
| 1 | | | | |
| 2 | QuEChERS | Acetonitrile | | LC-MS/MS |
| 3 | NT | | | |
| 4 | NT | | | |
| 5 | NT | | | |
| 6 | NT | | | |
| 7 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 8 | QuEChERS | Acetonitrile | Dispersive SPE | LC-MS/MS |
| 9 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 10 | NT | | | |
| 11 | QuEChERS | Acetonitrile (1% acetic acid) | C18 / PSA | LC-MS/MS |
| 12 | NT | | | |
| 13 | | | | |
| 14 | Solid-Liquid | DCM,Hex,Acetone | | LC-MS/MS |
| 15 | NT | | | |
| 16 | NT | | | |
| 17 | NT | | | |
| 18 | NT | | | |
| 19 | QuEChERS | ACN | d-SPE | LC-MS/MS |
| 20 | NT | | | |

Table 61 Sample S4 Green Bean Carbendazim Methodology

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|
| 1 | | | | |
| 2 | QuEChERS | Acetonitrile | | LC-MS/MS |
| 3 | NT | | | |
| 4 | NT | | | |
| 5 | NT | | | |
| 6 | NT | | | |
| 7 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 8 | QuEChERS | Acetonitrile | Dispersive SPE | LC-MS/MS |
| 9 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 10 | QuEChERS | ACN | PSA | LC-MS/MS |
| 11 | QuEChERS | Acetonitrile (1% acetic acid) | C18 / PSA | LC-MS/MS |
| 12 | NT | | | |
| 13 | | | | |
| 14 | Solid-Liquid | DCM,Hex,Acetone | | LC-MS/MS |
| 15 | NT | | | |
| 16 | | | | |
| 17 | NT | | | |
| 18 | NT | | | |
| 19 | QuEChERS | ACN | d-SPE | LC-MS/MS |
| 20 | QuEChERS | acetonitrile | Dispersive Solid Phase Extraction (d-spe) | LC-MSMS |

Table 62 Sample S4 Green Bean Omethoate Methodology

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|
| 1 | | | | |
| 2 | QuEChERS | Acetonitrile | | LC-MS/MS |
| 3 | Quechers | Acetonitrile | | GC-FPD |
| 4 | NT | | | |
| 5 | QuEChERS | 1%Acetic acid/Acetonitrile | Dispersive SPE | GC-MS |
| 6 | | | | |
| 7 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 8 | QuEChERS | Acetonitrile | Dispersive SPE | LC-MS/MS |
| 9 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 10 | NT | | | |
| 11 | QuEChERS | Acetonitrile (1% acetic acid) | C18 / PSA | LC-MS/MS |
| 12 | QuEChERS | Acetonitrile | dispersive-SPE | GC-FPD |
| 13 | QuEChERS | Acetonitrile | Florisil | GC-FPD |
| 14 | Solid-Liquid | DCM,Hex,Acetone | | GCMSMS &LCMSMS |
| 15 | NT | | | |
| 16 | NT | | | |
| 17 | NT | | | |
| 18 | NT | | | |
| 19 | QuEChERS | ACN | d-SPE | LC-MS/MS |
| 20 | QuEChERS | acetonitrile | Dispersive Solid Phase Extraction (d-spe) | GC-FPD |

Table 63 Sample S4 Green Bean Pyraclostrobin Methodology

| Lab. Code | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|
| 1 | | | | |
| 2 | QuEChERS | Acetonitrile | | LC-MS/MS |
| 3 | NT | | | |
| 4 | NT | | | |
| 5 | NT | | | |
| 6 | NT | | | |
| 7 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 8 | QuEChERS | Acetonitrile | Dispersive SPE | LC-MS/MS |
| 9 | QuEChERS | Acetonitrile | PSA | LC-MS/MS |
| 10 | QuEChERS | ACN | PSA | LC-MS/MS |
| 11 | QuEChERS | Acetonitrile (1% acetic acid) | C18 / PSA | LC-MS/MS |
| 12 | NT | | | |
| 13 | | | | |
| 14 | Solid-Liquid | DCM,Hex,Acetone | | LC-MS/MS |
| 15 | NT | | | |
| 16 | QuEChERS | Acetonitrile | dSPE | LC-MS/MS |
| 17 | NT | | | |
| 18 | NT | | | |
| 19 | QuEChERS | ACN | d-SPE | LC-MS/MS |
| 20 | NT | | | |

## APPENDIX 5 ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| 2,4-D | 2,4-Dichlorophenoxyacetic acid |
| 2D | Two-Dimensional |
| ACE | Acetone |
| ACN | Acetonitrile |
| AMPA | Aminomethylphosphonic acid |
| AV | Assigned Value |
| 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 |
| HEX | Hexane |
| HPLC | High Pressure Liquid Chromatography |
| 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 |
| LOQ | Limit of Quantitation |
| 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 |
| NMI | National Measurement Institute, Australia |

| | |
|---|---|
| No. | Number |
| NPD | Nitrogen Phosphorus Detection |
| NR | Not Reported |
| NT | Not Tested |
| p,p'-DDT | Dichlorodiphenyltrichloroethane |
| PCV | Performance Coefficient of Variation |
| PSA | Primary/Secondary Amine |
| PT | Proficiency Test |
| QuEChERS | Quick, Easy, Cheap, Effective, Rapid and Safe extraction |
| RA | Robust Average |
| Rec | Recovery |
| RM | Reference Material |
| RT | Room Temperature |
| RV | Reference Value |
| $s_{an}$ | Analytical standard deviation |
| $s_{sam}$ | Between-sample standard deviation |
| 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) |
| u | Standard Uncertainty |
| U | Expanded Uncertainty |
| UPLC | Ultra Performance Liquid Chromatography |
| WHO | World Health Organization |
| X | Assigned Value |
| $\chi$ | Participant Result |
| σ | Target standard deviation for proficiency assessment |

**END OF REPORT**