Australian Government
Department of Industry, Science and Resources

National Measurement Institute

Proficiency Test Final Report AQA 26-02 Pesticides in Fruit, Vegetables, and Hemp

June 2026

Our purpose is to help the government build a better future for all Australians through enabling a productive, resilient and sustainable economy, enriched by science and technology.

measurement.gov.au

© Commonwealth of Australia 2026.

Unless otherwise noted, the Commonwealth owns the copyright (and any other intellectual property rights, if any) in this publication.

All material in this publication is provided under a Creative Commons Attribution 4.0 International Licence (CC BY 4.0), with the exception of:

- the Commonwealth Coat of Arms;
- the logo of the Department of Industry, Science and Resources;
- photographs of our staff and premises; and
- content supplied by third parties.

Creative Commons Attribution 4.0 International Licence is a standard form licence agreement that allows you to copy, distribute, transmit and adapt this publication provided you attribute the work. A summary of the licence terms is available at: creativecommons.org/licenses/by/4.0/. Further details are available on the Creative Commons website, at: creativecommons.org/licenses/by/4.0/legalcode.

You may not copy, distribute, transmit or adapt any material in this publication in any way that suggests that this department or the Commonwealth endorses you or any of your services or products.

Attribution

Material contained in this publication is to be attributed to this department as:

© Commonwealth of Australia, Department of Industry, Science and Resources, Proficiency Test Final Report AQA 26-02 Pesticides in Fruit, Vegetables, and Hemp, 2026.

Third party copyright

Wherever a third party holds copyright in material contained in this publication, the copyright remains with that party. Their permission may be required to use the material.

This department has made all reasonable efforts to:

- clearly label material where the copyright is owned by a third party;
- ensure that the copyright owner has consented to this material being contained in this publication.

Using the Commonwealth Coat of Arms

The terms of use for the Coat of Arms are available on the Department of Prime Minister and Cabinet's website, at www.pmc.gov.au/resource-centre/government/commonwealth-coat-arms-information-and-guidelines

ACKNOWLEDGMENTS

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

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

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

Jenny Xu

Geoff Morschel

Jasmine Duong

Hamish Lenton

Aaron Mamo

Sofia Racomelara

Zoë Baker-Moss

Scott Chen

Gabriela Saveluc

Grace Pattanadarong

Hao Nguyen

Georgios Dabos

I would also like to thank the members of the Pesticides in Fruit and Vegetables PT Advisory group for their input in the design of this PT study.

Luminita Antin

A/g Manager, Chemical Reference Values

105 Delhi Rd, North Ryde, NSW 2113, Australia

Phone: +61 2 9449 0234

Email: proficiency@measurement.gov.au

Accredited for compliance with ISO/IEC 17043

Accreditation No. 198; Site No. 14485

TABLE OF CONTENTS

SUMMARY 1
1 INTRODUCTION 3
1.1 NMIA Proficiency Testing Program 3
1.2 Study Aims 3
1.3 Study Conduct 3
2 STUDY INFORMATION 4
2.1 Study Timetable 4
2.2 Participation and Laboratory Code 4
2.3 Selection of Pesticides and Matrices, and Test Material Preparation 4
2.4 Homogeneity and Stability of Test Materials 5
2.5 Sample Storage, Dispatch and Receipt 5
2.6 Instructions to Participants 6
2.7 Interim Report and Preliminary Report 7
3 PARTICIPANT LABORATORY INFORMATION 8
3.1 Test Methods Reported by Participants 8
3.2 Basis of Participants' Measurement Uncertainty Evaluation 8
3.3 Participants' Comments 10
4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS 11
4.1 Results Summary 11
4.2 Outliers and Extreme Outliers 11
4.3 Assigned Value 11
4.4 Robust Average and Robust Between-Laboratory Coefficient of Variation 11
4.5 Performance Coefficient of Variation 11
4.6 Standard Deviation for Proficiency Assessment 12
4.7 z-Score 12
4.8 E_n-Score 12
4.9 Traceability and Measurement Uncertainty 12
5 TABLES AND FIGURES 13
6 DISCUSSION OF RESULTS 67
6.1 Assigned Value 67
6.2 Measurement Uncertainty Reported by Participants 68
6.3 z-Scores 68
6.4 E_n-Scores 71
6.5 Range of Pesticides Analysed by Participants 72
6.6 False Negatives 72
6.7 Reporting of Additional Analytes 73
6.8 Summary of Participants' Results and Performances 73
6.9 Participants' Results and Analytical Methods 77
6.10 Certified Reference Materials 91
6.11 Effect of Sample Matrix 91
6.12 Fitness for Purpose of Pesticide Results 92
6.13 Comparison with Previous Pesticides in Food PT Studies 99
7 REFERENCES 102

APPENDIX 1 SAMPLE PREPARATION 104
APPENDIX 2 HOMOGENEITY AND STABILITY ASSESSMENT 105
A2.1 Homogeneity 105
A2.2 Stability 107
APPENDIX 3 ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY, z-SCORE AND E_n-SCORE CALCULATIONS 111
A3.1 Robust Average and Associated Uncertainty 111
A3.2 z-Score and E_n-Score Calculation 111
APPENDIX 4 PARTICIPANTS' TEST METHODS 112
A4.1 METHODOLOGY FOR S1 TOMATO 112
A4.2 METHODOLOGY FOR S2 BLUEBERRY 124
A4.3 METHODOLOGY FOR S3 HEMP FLOUR 139
A4.4 METHODOLOGY FOR S4 GARLIC 151
APPENDIX 5 ACRONYMS AND ABBREVIATIONS 152

SUMMARY

This report presents the results of proficiency test AQA 26-02 Pesticides in Fruit, Vegetables, and Hemp. This study also included a pilot sample which was focused on the measurement of maleic hydrazide in garlic; this sample was designed to enable laboratories to develop their methods for this test.

Seventeen laboratories registered to participate, and all submitted results.

The sample set consisted of 4 samples: Samples were prepared by adding a range of pesticide standard solutions to tomatoes (Sample S1), blueberries (Sample S2) and hemp flour (Sample S3). The pilot Sample S4 was garlic puree spiked with maleic hydrazide.

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

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 participants' ability to correctly identify pesticides in fruit, vegetables, and hemp.*

Laboratories 4, 5, 6, 9, and 12 reported numeric results for all 20 scored analytes across all three samples.
Eight participants (Laboratories 1, 2, 4, 7, 8, 10, 15, and 16) did not report results for analytes that they tested for and were present in the test samples (total of 13 results).

- *Compare participant's performances and assess their capabilities in the measurement of pesticides in fruit, vegetables, and hemp.*

Of 220 results for which z-scores were calculated, 194 (88%) returned $|z| \leq 2.0$, indicating an acceptable performance.

Of 218 results for which E_n-scores were calculated, 181 (83%) returned $|E_n| < 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratory 4 achieved acceptable z-scores and E_n-scores for all scored analytes.

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

Food Standards Australia and New Zealand (FSANZ) specifies maximum residue limits (MRLs) for various pesticides in different food products. Most participants' results in this study correctly reflected compliance or non-compliance with FSANZ MRLs.

The concentrations of buprofezin and indoxacarb in the tomato sample were close to the relevant MRLs. In some cases, unsuitable evaluation of uncertainty associated with reported results may have led to the sample being incorrectly deemed as inconclusive, which could trigger requests for further testing and result in additional expenses.

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

Although Sample S3 hemp flour was a significantly different matrix in comparison to Samples S1 tomato and S2 blueberry, the majority of participants used the same procedure for the analysis of all samples.

The most common methodology was extraction using the QuEChERS procedure, with acetonitrile as the extraction solvent. Both GC and LC techniques were used, depending on the analyte.

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

Of 269 numeric results reported for the analytes of interest, 265 (99%) were reported with an associated expanded measurement uncertainty. The magnitude of the reported uncertainties was within the range 3.5% to 200% relative.

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

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

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

1 INTRODUCTION

1.1 NMIA Proficiency Testing Program

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

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

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

1.2 Study Aims

The aims of the study were to:

- assess participants' ability to correctly identify pesticides in fruit, vegetables, and hemp;
- compare participants' performances and assess their capabilities in the measurement of pesticides in fruit, vegetables, and hemp;
- assess participants' ability to determine compliance of pesticides in fruit, vegetables, and hemp against regulatory standards;
- evaluate participants' methods for the measurement of pesticides in fruit, vegetables, and hemp;
- develop the practical application of measurement uncertainty, and provide participants with information that will be useful in assessing their uncertainty evaluations; and
- produce materials that can be used in method validation and as control samples.

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

1.3 Study Conduct

The conduct of NMIA proficiency tests is described in the NMIA Study Protocol for Proficiency Testing.[2] The statistical methods used are described in the NMIA 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]

NMIA is accredited by the National Association of Testing Authorities, Australia (NATA) to ISO/IEC 17043 as a provider of proficiency testing schemes. This study falls within the scope of NMIA's accreditation (Accreditation No. 198; Site No. 14485).

2 STUDY INFORMATION

2.1 Study Timetable

The timetable of the study was:

Invitations sent 15 December 2025

Samples sent 23 February 2026

Results due 20 March 2026

Interim Report 26 March 2026

Preliminary Report 31 March 2026

2.2 Participation and Laboratory Code

Seventeen laboratories registered to participate, and all were assigned a confidential laboratory code number. All participants submitted results.

2.3 Selection of Pesticides and Matrices, and Test Material Preparation

For pesticide and matrix selection, consideration was given to:

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

Samples were prepared by adding pesticide standard solutions to pureed tomatoes (Sample S1), blueberries (Sample S2), hemp flour (Sample S3), and garlic (Sample S4, pilot sample).

The spiked values for the samples and corresponding Australian MRLs from the FSANZ Food Standards Code are presented in Table 1.[5]

Table 1 Spiked Values and MRLs of Test Samples

Sample	Analyte	Spiked Value (mg/kg)	MRL* (mg/kg)
S1 (Tomato)	Abamectin	0.0305	0.1
	Acephate	0.0504	5
	Buprofezin	0.856	1
	Endosulfan sulfate	0.0398	-
	Fenvalerate	0.0607	0.2
	Imidacloprid	0.0200	0.5
	Indoxacarb	0.300	0.2
	Methomyl	0.700	1
S2 (Blueberries)	Chlorpyrifos	0.0302	0.01
	Cyprodinil	0.0615	3
	Dimethoate	0.497	5
	Imidacloprid	0.0198	3.5

Sample	Analyte	Spiked Value (mg/kg)	MRL* (mg/kg)
	Maldison (Malathion)	1.97	10
	Methomyl	0.694	2
	Phosmet	3.98	10
	Thiometon	1.98	-
S3 (Hemp Flour)	AMPA	3.01	0.1
	Azoxystrobin	0.892	0.1
	Chlordane	0.199	-
	Cypermethrin	2.01	0.1
	Diazinon	0.995	-
	Difenoconazole	0.150	0.02
	Indoxacarb	0.307	0.05
	Maldison (Malathion)	1.95	0.05
	Profenofos	0.198	0.02
S4 (Garlic)	Maleic hydrazide	12.9	15

*MRLs for Sample S3 are for hempseed. Some MRLs are for the sum of several different permitted residues,[5] however for this study participants were requested to report results only for the named analyte.

Additional sample preparation details are provided in Appendix 1.

2.4 Homogeneity and Stability of Test Materials

For Samples S1 and S2, the process used to prepare, store and dispatch the test samples has been demonstrated to produce sufficiently homogeneous and stable samples for previous NMIA PT studies of similar analytes and matrices. Reports in the Joint FAO/WHO Meeting on Pesticide Residues (JMPR) database, also gave some assurance that various pesticides would be stable in frozen produce.[6]

Analytes have only been scored where the results returned by participants gave no reason to question the homogeneity or stability.

Sample S3 hemp flour was a new matrix introduced in this study, and so homogeneity and stability testing was conducted for this sample. Samples were demonstrated to be sufficiently homogeneous and stable for the purposes of this PT study.

Sample S4 was a pilot sample. The process used to prepare this sample has been demonstrated to produce sufficiently homogeneous samples. No stability testing was conducted for this sample.

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

2.5 Sample Storage, Dispatch and Receipt

After preparation, the samples were stored in a freezer at -20°C. Participants were sent 100 g portions of both spiked and unspiked Samples S1 and S2, and 20 g portions of both spiked and unspiked Samples S3 and S4. The samples were packaged into insulated polystyrene foam boxes with cooler bricks and dispatched by courier on 23 February 2026.

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.

2.6 Instructions to Participants

Participants were provided with a list of analytes that were potentially spiked into the samples (Table 2).

Table 2 List of Possible Analytes

Sample S1 Tomato	Abamectin	Dicofol	Indoxacarb
	Acephate	Endosulfan Sulfate	Iprodione
	Buprofezin	Fenhexamid	Metalaxyl
	Carbendazim	Fenitrothion	Methamidophos
	Chlorothalonil	Fenvalerate	Methomyl
	Cyhalothrin	Imazalil	Oxamyl
	Cypermethrin	Imidacloprid	Permethrin
Sample S2 Blueberry	Abamectin	Cyprodinil	Maldison (Malathion)
	Acetamiprid	2,4-D	Metalaxyl
	Azinphos-methyl	Difenoconazole	Methomyl
	Bifenthrin	Dimethoate	Phosmet
	Chlorpyrifos	Fenhexamid	Pyraclostrobin
	Clothianidin	Imidacloprid	Spirotetramat
	Cypermethrin	Iprodione	Thiometon
Sample S3 Hemp Flour	AMPA	Cypermethrin	Glyphosate
	Azinphos-methyl	Deltamethrin	Indoxacarb
	Azoxystrobin	Diazinon	Maldison (Malathion)
	Bromoxynil	Difenoconazole	Metalaxyl
	Chlorantraniliprole	Fenitrothion	Profenofos
	Chlordane	Fipronil	Sethoxydim
	Cyfluthrin	Fludioxonil	Spinosad
Sample S4 Garlic	Maleic hydrazide		

Participants were instructed as follows:

- If the samples cannot be analysed immediately, please store them frozen.
- Quantitatively analyse the samples using your routine test method.
- The unspiked material need not be analysed, it is provided for participants to use if they wish.
- Participants need not test for all analytes listed.
- Please analyse the samples immediately after thawing and mixing thoroughly.

- For each analyte in each sample report a single result on as received basis in units of mg/kg expressed as if reporting to a client (i.e. corrected for recovery or not, according to your standard procedure). This figure will be used in all statistical analysis in the study report.
- For each analyte in each sample report the associated expanded measurement uncertainty (e.g. 0.50 ± 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 evaluation as requested by the results sheet emailed to you.
- If determined, report your percentage recovery. This will be presented in the report for information only.
- Sample S4 Garlic is a pilot sample, and no individual performance assessment will be made. However, participants will still be able to compare their results to other participants' results and the spiked value.
- Return the completed results sheet by 20 March 2026 by email to proficiency@measurement.gov.au.

Additionally, participants were provided with special handling instructions for Sample S4 garlic: 'If Sample S4 Garlic has arrived already defrosted, please immediately aliquot the required amounts for each analysis and freeze the aliquots separately. If the sample has arrived frozen, please aliquot and freeze separately when you first defrost the bulk sample. Ensure that this sample does not go above 4°C for any extended period, and avoid freeze-thaw cycles of the bulk sample.'

2.7 Interim Report and Preliminary Report

An Interim Report was emailed to all participants on 26 March 2026.

A Preliminary Report was emailed to all participants on 31 March 2026. This report included a summary of the results reported by participants, assigned values, performance coefficients of variation (PCVs), *z*-scores and E_n-scores for each analyte in this study. No data from the Preliminary Report has been changed in the present Final Report.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Test Methods Reported by Participants

Participants were requested to provide information about their test methods. Responses received are presented in Appendix 4. Some responses may be modified so that the participant cannot be identified.

3.2 Basis of Participants' Measurement Uncertainty Evaluation

Participants were requested to provide information about their basis of measurement uncertainty (MU). Responses are presented in Tables 3 and4. Some responses may be modified so that the participant cannot be identified.

Table 3 Basis of MU Evaluation

Lab. Code	Approach to Evaluating MU	Information Sources for MU Evaluation*		Guide Document for Evaluating MU
		Precision	Method Bias	
1	Top Down - precision and evaluations of the method and laboratory bias k = 1.96	Control samples - SS Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS Standard purity	SANTE 12682/2019
2	Standard deviation of replicate analyses multiplied by 2 or 3 Coverage factor not reported	Control samples - SS Duplicate analysis	CRM Instrument calibration Laboratory bias from PT studies	Eurolab Technical Report 1/2007
3	Top Down - precision and evaluations of the method and laboratory bias k = 2	Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS Standard purity	Codex CAC/GL 59-2006 "Guidelines on Estimation of Uncertainty of Results"
4	Horwitz formula k = 2	Control samples - SS Duplicate analysis	Instrument calibration Recoveries of SS Standard purity	NMIA Uncertainty Course
5	Top Down - precision and evaluations of the method and laboratory bias Coverage factor not reported	Control samples Duplicate analysis Instrument calibration	Instrument calibration Laboratory bias from PT studies Recoveries of SS Standard purity	ISO/GUM
6	Coverage factor not reported	Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS Standard purity	NMIA Uncertainty Course
7	Top Down - precision and evaluations of the method and laboratory bias Coverage factor not reported	Control samples - SS	CRM Standard purity	ISO/GUM

Lab. Code	Approach to Evaluating MU	Information Sources for MU Evaluation*		Guide Document for Evaluating MU
		Precision	Method Bias	
8	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control samples - SS Duplicate analysis	Recoveries of SS	NMIA Uncertainty Course
9	Top Down - precision and evaluations of the method and laboratory bias k = 2	Duplicate analysis Instrument calibration	CRM Recoveries of SS Standard purity	Eurachem/CITAC Guide
10	Top Down - precision and evaluations of the method and laboratory bias k = 2 (reported as 95%)	Control samples - CRM Duplicate analysis	Recoveries of SS	ISO/GUM
11	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control samples - SS Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	SANTE 12682/2019
12	Top Down - precision and evaluations of the method and laboratory bias Coverage factor not reported	Control samples - SS Duplicate analysis	CRM	Eurachem/CITAC Guide
13**	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control samples - SS	Recoveries of SS Standard purity	SANTE 12682/2019
14	Top-down approach k = 2	Duplicate analysis	CRM Instrument calibration Recoveries of SS Standard purity	SANTE 12682/2019
15	Top Down - precision and evaluations of the method and laboratory bias k = 2	Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
16	Standard deviation of replicate analyses multiplied by 2 or 3 k = 2	Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS Standard purity	Eurachem/CITAC Guide
17	Top Down - precision and evaluations of the method and laboratory bias Coverage factor not reported	Control samples - SS Duplicate analysis	Recoveries of SS Standard purity	SANTE 12682/2019

*CRM = Certified Reference Material; SS = Spiked Samples. **Additional information in Table 4.

Table 4 Uncertainty Evaluation Additional Information

Lab. Code	Comments for Approach to Evaluating MU
13	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%.

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 are presented in Table 5. Some responses may be modified so that the participant cannot be identified.

Table 5 Participants' Comments

Lab. Code	Sample	Participant's Comments	Study Coordinator's Response
4	All	Note GCMS and LCMS results were averaged for some analytes, but methodology sample table does not allow you to put in 2 method ids from template, e.g. Malathion was calculated using LCMS, GCMS and ECD results for comparison.	Thank you for your feedback. We will review the design of our results form. We have requested participants to only report the methodology used to produce the result reported, and the results sheet has been set-up to allow for one methodology per analyte by default. However, if multiple methods have been used, the cells are able to be over-written, or otherwise we suggest participants to add comments in the additional information field.
8	S3	Our analytical suite is based on the European Pharmacopoeia guidelines for medicinal cannabis products. We do not cover many of the compounds listed above	Thank you for your feedback. Analytes were selected with consideration to a variety of factors, as noted in Section 2.3. Several analytes from the European Pharmacopoeia guidelines were included in this study. We will make sure to include other analytes from these guidelines too in our future PT studies.

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 6 to 32, with summary statistics and other estimates of analyte mass fraction. Bar charts of results and performance scores are presented in Figures 2 to 28. An example chart with interpretation guide is shown in Figure 1.

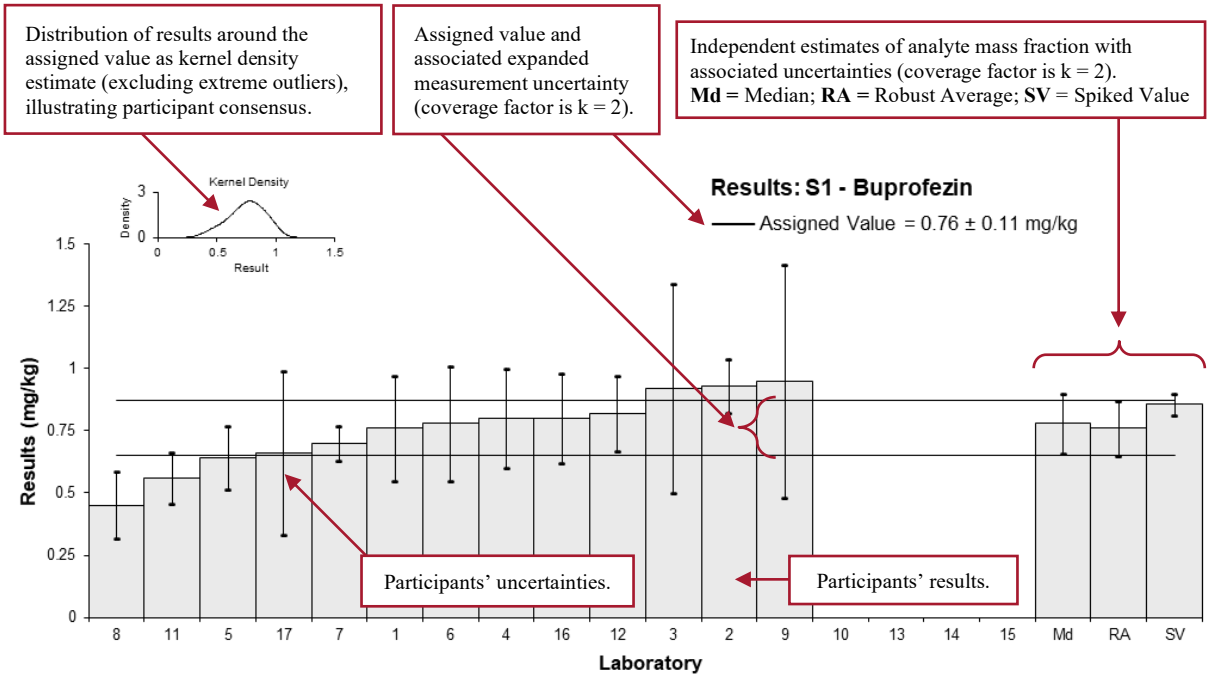


Figure 1 Guide to Presentation of Results

4.2 Outliers and Extreme Outliers

Outliers were results less than 50% and greater than 150% of the robust average, and these were removed before the calculation of the assigned value (when using the robust average).[3,4] Extreme outliers were obvious blunders, e.g. results reported with incorrect units or for a different analyte, and such results were removed for the calculation of all statistics.[3,4]

4.3 Assigned Value

The assigned value is defined as the 'value attributed to a particular property or characteristic of a proficiency testing item'.[1] In this PT study, this property is the mass fraction of the analytes in the samples. The assigned values for all scored analytes were the robust averages of participants' results, and the expanded uncertainties were evaluated from the associated robust SDs (Appendix 3).

4.4 Robust Average and Robust Between-Laboratory Coefficient of Variation

The robust averages and associated expanded MUs, and robust CVs (a measure of the variability of participants' results) were calculated using the procedure described in ISO 13528.[7] Robust CV as presented in the Section 5 (Statistics table) is the robust between-laboratory CV including outliers but excluding extreme outliers. Everywhere else in the report, the robust between-laboratory CV refers to the robust CV calculated with both outliers and extreme outliers removed.

4.5 Performance Coefficient of Variation

The performance coefficient of variation (PCV) is a set 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 realistic value for the PCV, a participant's performance does not depend on other participants' performance, and can be compared from study to study when the PCV remains the same.

4.6 Standard Deviation for Proficiency Assessment

The standard deviation for proficiency assessment (σ, SDPA) 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

χ is a participant's result

X is the assigned value

σ is the SDPA from Equation 1

For the absolute value of a z-score: $|z| \leq 2.0$ is acceptable; $2.0 < |z| < 3.0$ is questionable; and $|z| \geq 3.0$ is not acceptable.

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

4.8 E_n-Score

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

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

where:

E_n is E_n-score

χ is a participant's result

X is the assigned value

U_χ is the expanded uncertainty of the participant's result

U_X is the expanded uncertainty of the assigned value

For the absolute value of an E_n-score: $|E_n| < 1.0$ is acceptable; and $|E_n| \geq 1.0$ is not acceptable.

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 6

Sample Details

Sample No.	S1
Matrix	Tomato
Analyte	Abamectin
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	NT	NT	NT
2	NT	NT	NT
3	NT	NT	NT
4	NR	NR	NR
5	0.013	0.0026	NR
6	NT	NT	NT
7	NT	NT	NT
8	0.02	0.006	81
9	0.030	0.015	99
10	NT	NT	NT
11	NT	NT	NT
12	0.024	0.010	110
13	NT	NT	NT
14	NT	NT	NT
15	NS	NS	NS
16	0.024	NR	82
17	0.030	0.015	85

Statistics

Assigned Value	Not Set	
Spike Value	0.0305	0.0015
Robust Average	0.0235	0.0075
Median	0.0240	0.0076
Mean	0.0235	
N	6	
Max	0.030	
Min	0.013	
Robust SD	0.0073	
Robust CV	31%	

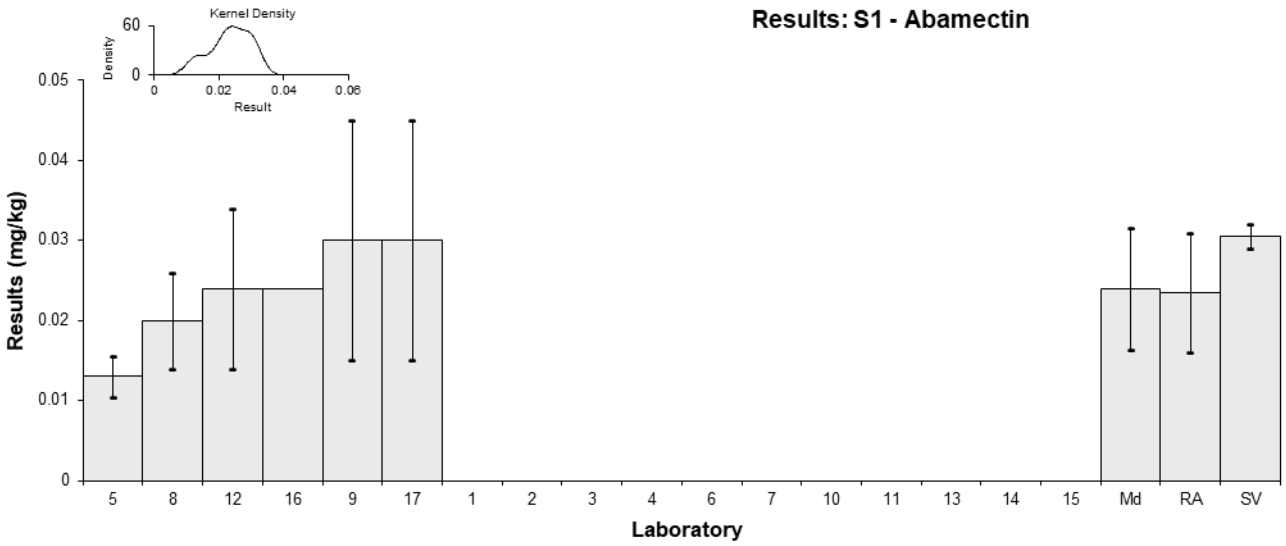

Results: S1 - Abamectin
Kernel Density
Density
60
0
0
0.02
0.04
0.06
Result
Results (mg/kg)
0.05
0.04
0.03
0.02
0.01
0
5
8
12
16
9
17
1
2
3
4
6
7
10
11
13
14
15
Md
RA
SV
Laboratory

Figure 2

Table 7

Sample Details

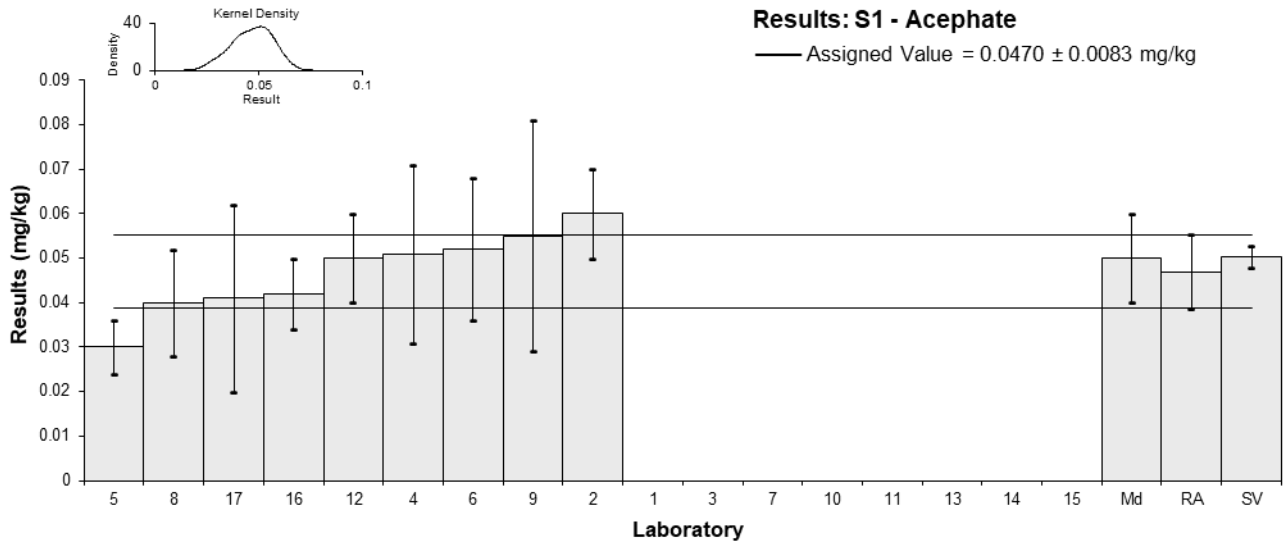
Sample No.	S1
Matrix	Tomato
Analyte	Acephate
Unit	mg/kg

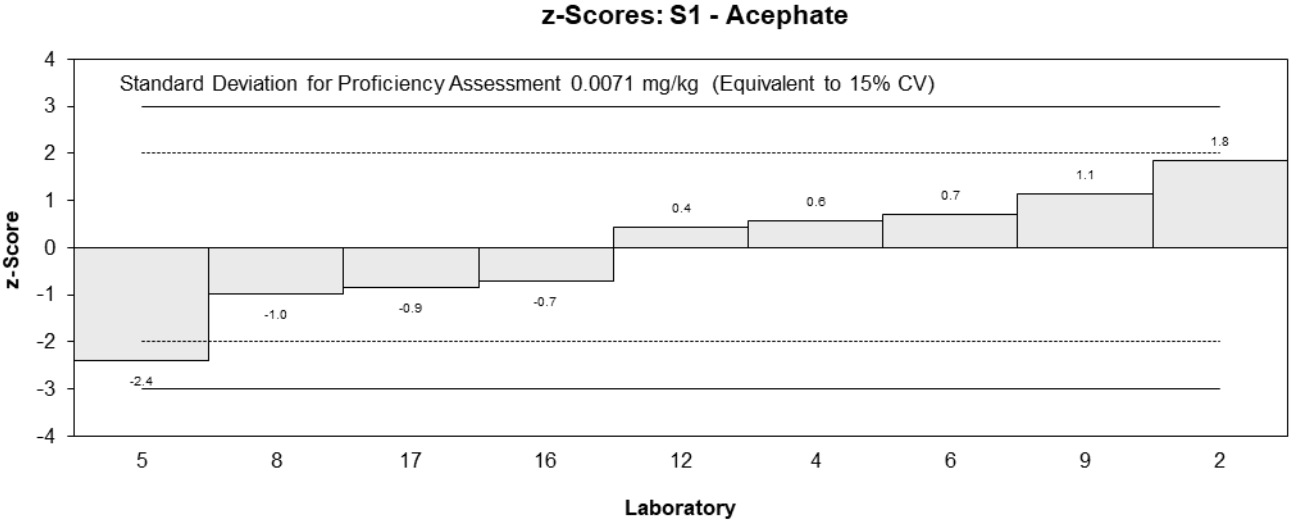
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	NT	NT	NT		
2	0.06	0.01	97	1.84	1.00
3	NT	NT	NT		
4	0.051	0.02	85	0.57	0.18
5	0.03	0.006	NR	-2.41	-1.66
6	0.052	0.016	91	0.71	0.28
7	NT	NT	NT		
8	0.04	0.012	81	-0.99	-0.48
9	0.055	0.026	57	1.13	0.29
10	NT	NT	NT		
11	NT	NT	NT		
12	0.050	0.010	96	0.43	0.23
13	NT	NT	NT		
14	NT	NT	NT		
15	NS	NS	NS		
16	0.042	0.008	78	-0.71	-0.43
17	0.041	0.021	81	-0.85	-0.27

Statistics

Assigned Value	0.0470	0.0083
Spike Value	0.0504	0.0025
Robust Average	0.0470	0.0083
Median	0.0500	0.0099
Mean	0.0468	
N	9	
Max	0.06	
Min	0.03	
Robust SD	0.0099	
Robust CV	21%	


Kernel Density
Density
Result
Results: S1 - Acephate
Assigned Value = 0.0470 ± 0.0083 mg/kg
Results (mg/kg)
Laboratory
5 8 17 16 12 4 6 9 2 1 3 7 10 11 13 14 15 Md RA SV


z-Scores: S1 - Acephate
Standard Deviation for Proficiency Assessment 0.0071 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
5 8 17 16 12 4 6 9 2
-2.4
-1.0
-0.9
-0.7
0.4
0.6
0.7
1.1
1.8

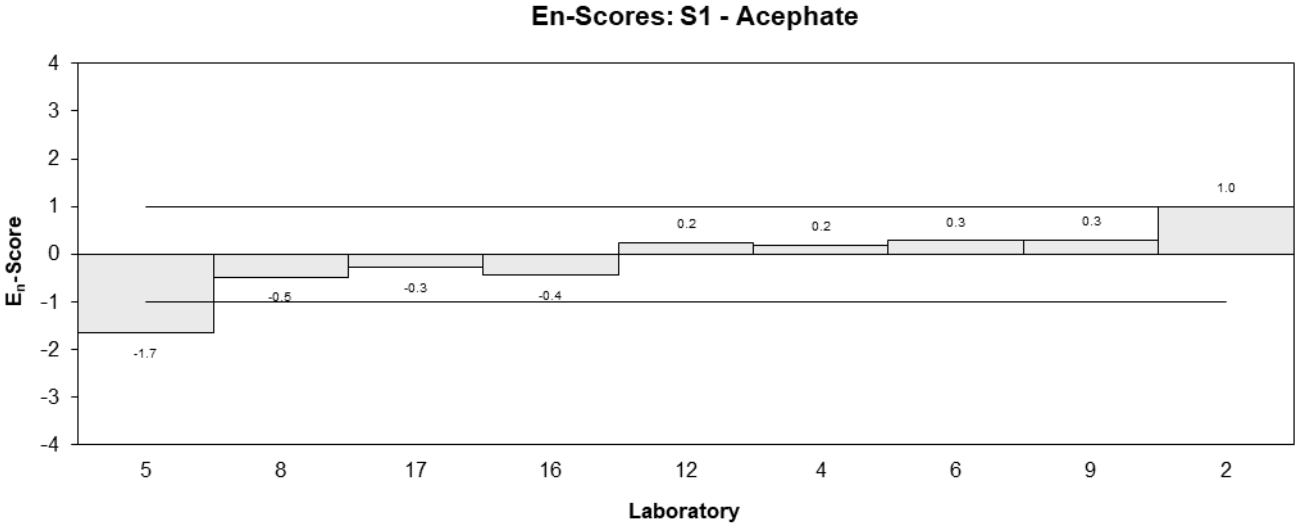

En-Scores: S1 - Acephate
En-Score
Laboratory
5 8 17 16 12 4 6 9 2
-1.7
-0.5
-0.3
-0.4
0.2
0.2
0.3
0.3
1.0

Figure 3

Table 8

Sample Details

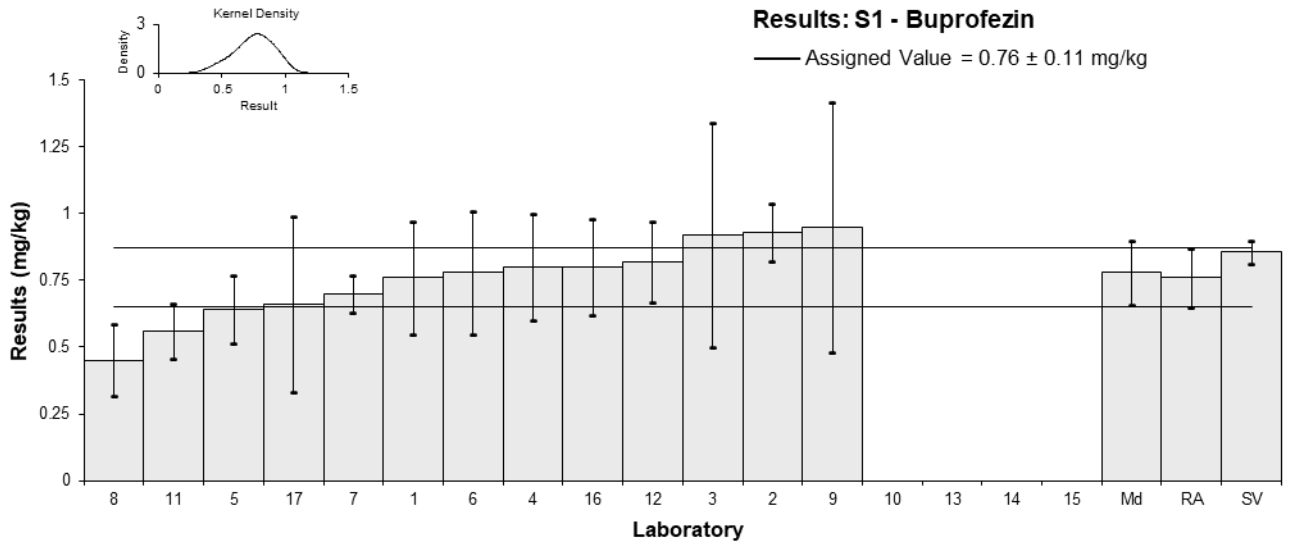
Sample No.	S1
Matrix	Tomato
Analyte	Buprofezin
Unit	mg/kg

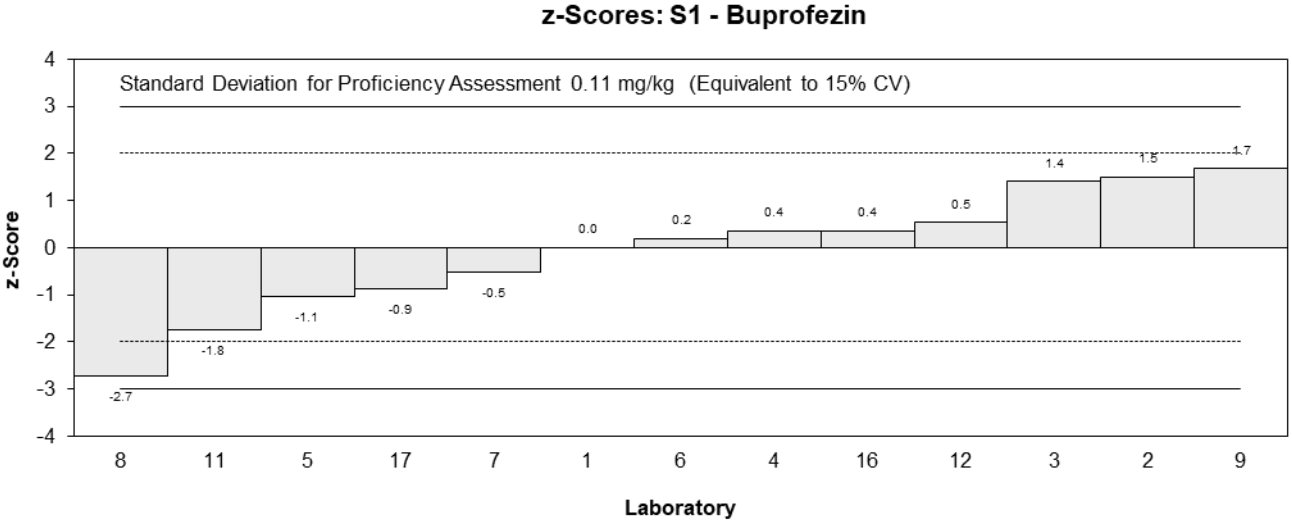
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.76	0.21	128	0.00	0.00
2	0.93	0.11	102	1.49	1.09
3	0.92	0.42	119	1.40	0.37
4	0.8	0.2	98	0.35	0.18
5	0.64	0.128	NR	-1.05	-0.71
6	0.78	0.23	88	0.18	0.08
7	0.70	0.07	100.67	-0.53	-0.46
8	0.45	0.135	79	-2.72	-1.78
9	0.95	0.47	90	1.67	0.39
10	NT	NT	NT		
11	0.560	0.101	88	-1.75	-1.34
12	0.82	0.15	93	0.53	0.32
13	NT	NT	NT		
14	NT	NT	NT		
15	NS	NS	NS		
16	0.801	0.18	67	0.36	0.19
17	0.66	0.33	88	-0.88	-0.29

Statistics

Assigned Value	0.76	0.11
Spike Value	0.856	0.043
Robust Average	0.76	0.11
Median	0.78	0.12
Mean	0.752	
N	13	
Max	0.95	
Min	0.45	
Robust SD	0.15	
Robust CV	20%	


Kernel Density
Density
Result
Results: S1 - Buprofezin
Assigned Value = 0.76 ± 0.11 mg/kg
Results (mg/kg)
Laboratory
8 11 5 17 7 1 6 4 16 12 3 2 9 10 13 14 15 Md RA SV


z-Scores: S1 - Buprofezin
Standard Deviation for Proficiency Assessment 0.11 mg/kg (Equivalent to 15% CV)
z-Score
-2.7 -1.8 -1.1 -0.9 -0.5 0.0 0.2 0.4 0.4 0.5 1.4 1.5 1.7
Laboratory
8 11 5 17 7 1 6 4 16 12 3 2 9

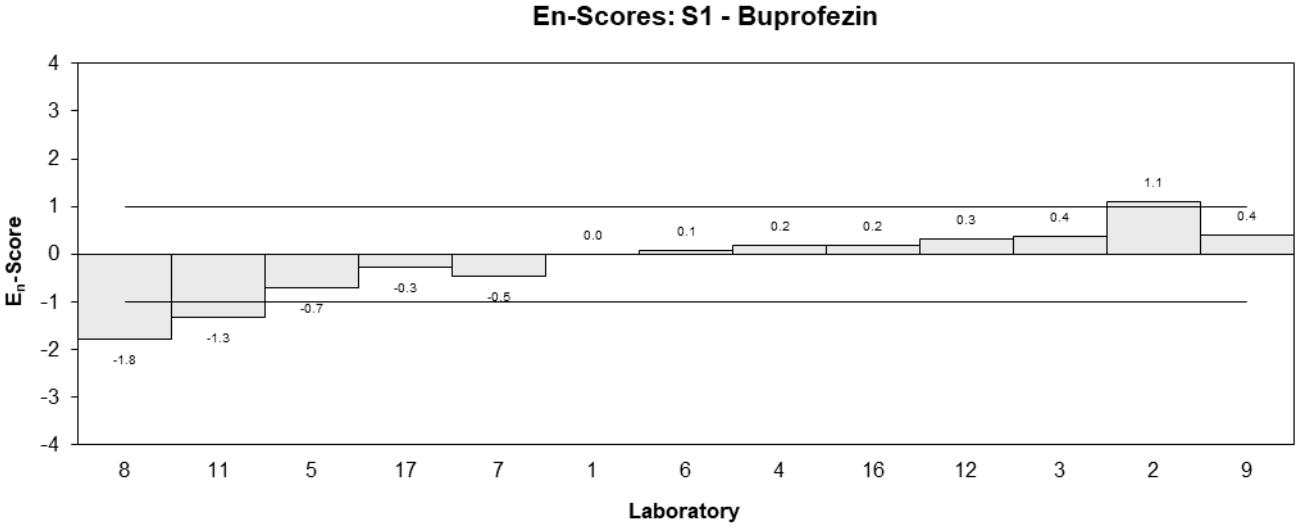

En-Scores: S1 - Buprofezin
En-Score
-1.8 -1.3 -0.7 -0.3 -0.5 0.0 0.1 0.2 0.2 0.3 0.4 1.1 0.4
Laboratory
8 11 5 17 7 1 6 4 16 12 3 2 9

Figure 4

Table 9

Sample Details

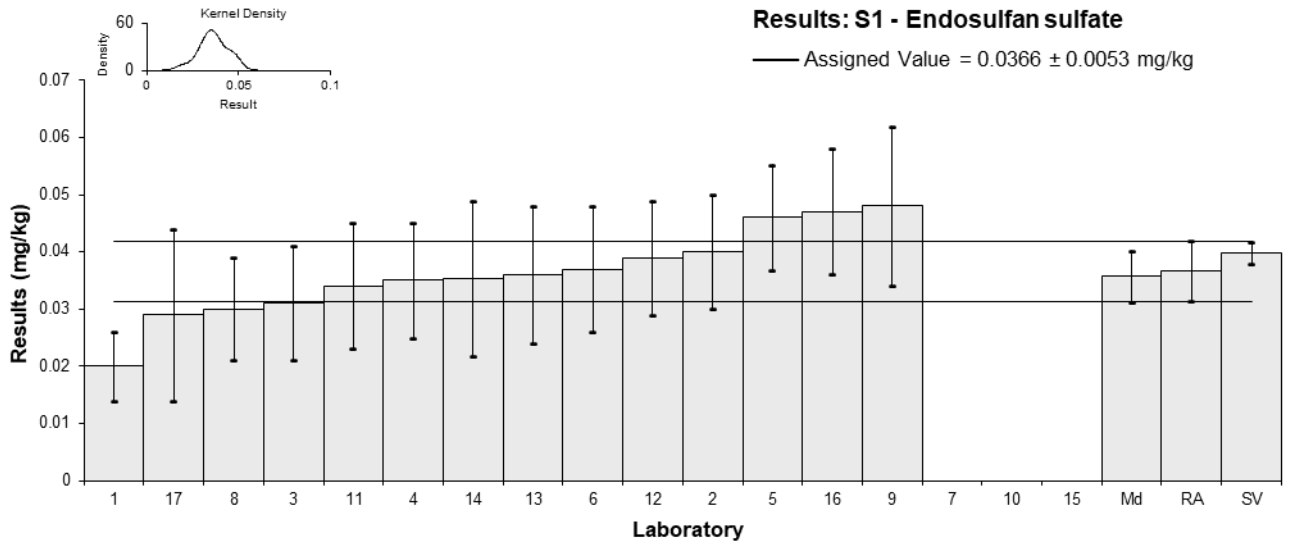
Sample No.	S1
Matrix	Tomato
Analyte	Endosulfan sulfate
Unit	mg/kg

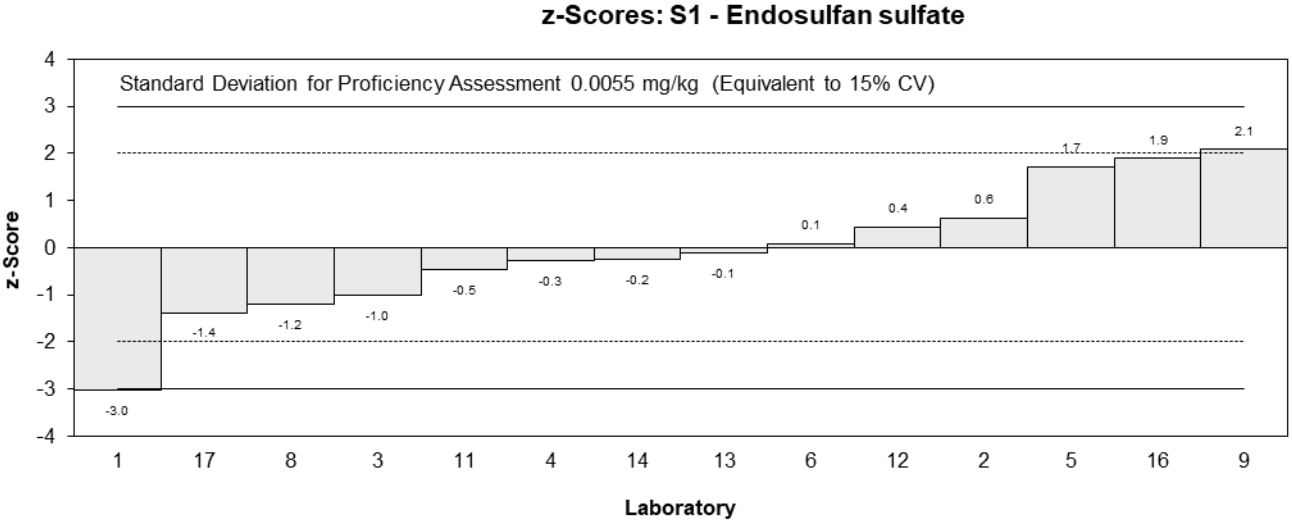
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.02	0.006	129	-3.02	-2.07
2	0.04	0.01	87	0.62	0.30
3	0.031	0.010	71	-1.02	-0.49
4	0.035	0.01	104	-0.29	-0.14
5	0.046	0.0092	NR	1.71	0.89
6	0.037	0.011	88	0.07	0.03
7	NT	NT	NT		
8	0.03	0.009	68	-1.20	-0.63
9	0.048	0.014	102	2.08	0.76
10	< 0.05	NR	NR		
11	0.034	0.011	85	-0.47	-0.21
12	0.039	0.010	78	0.44	0.21
13	0.036	0.012	95	-0.11	-0.05
14	0.0353	0.0136	105	-0.24	-0.09
15	NS	NS	NS		
16	0.047	0.011	104	1.89	0.85
17	0.029	0.015	112	-1.38	-0.48

Statistics

Assigned Value	0.0366	0.0053
Spike Value	0.0398	0.0020
Robust Average	0.0366	0.0053
Median	0.0357	0.0045
Mean	0.0362	
N	14	
Max	0.048	
Min	0.02	
Robust SD	0.0079	
Robust CV	22%	


Kernel Density
Density
Result
Results: S1 - Endosulfan sulfate
Assigned Value = 0.0366 ± 0.0053 mg/kg
Results (mg/kg)
Laboratory
1 17 8 3 11 4 14 13 6 12 2 5 16 9 7 10 15 Md RA SV


z-Scores: S1 - Endosulfan sulfate
Standard Deviation for Proficiency Assessment 0.0055 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
1 17 8 3 11 4 14 13 6 12 2 5 16 9
-3.0 -1.4 -1.2 -1.0 -0.5 -0.3 -0.2 -0.1 0.1 0.4 0.6 1.7 1.9 2.1

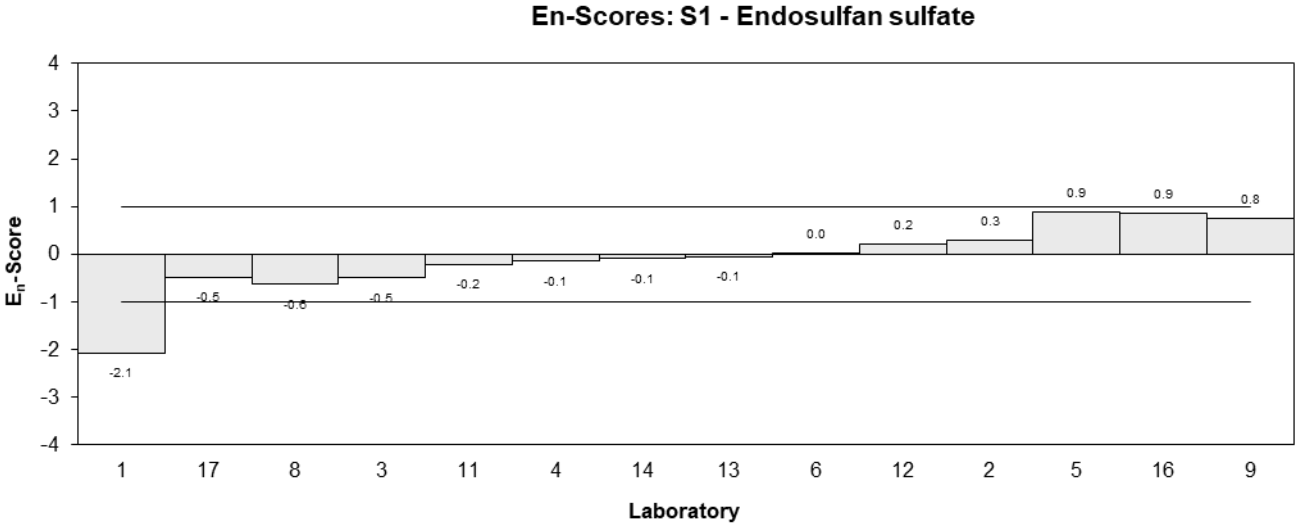

En-Scores: S1 - Endosulfan sulfate
En-Score
Laboratory
1 17 8 3 11 4 14 13 6 12 2 5 16 9
-2.1 -0.5 -0.6 -0.5 -0.2 -0.1 -0.1 -0.1 0.0 0.2 0.3 0.9 0.9 0.8

Figure 5

Table 10

Sample Details

Sample No.	S1
Matrix	Tomato
Analyte	Fenvalerate
Unit	mg/kg

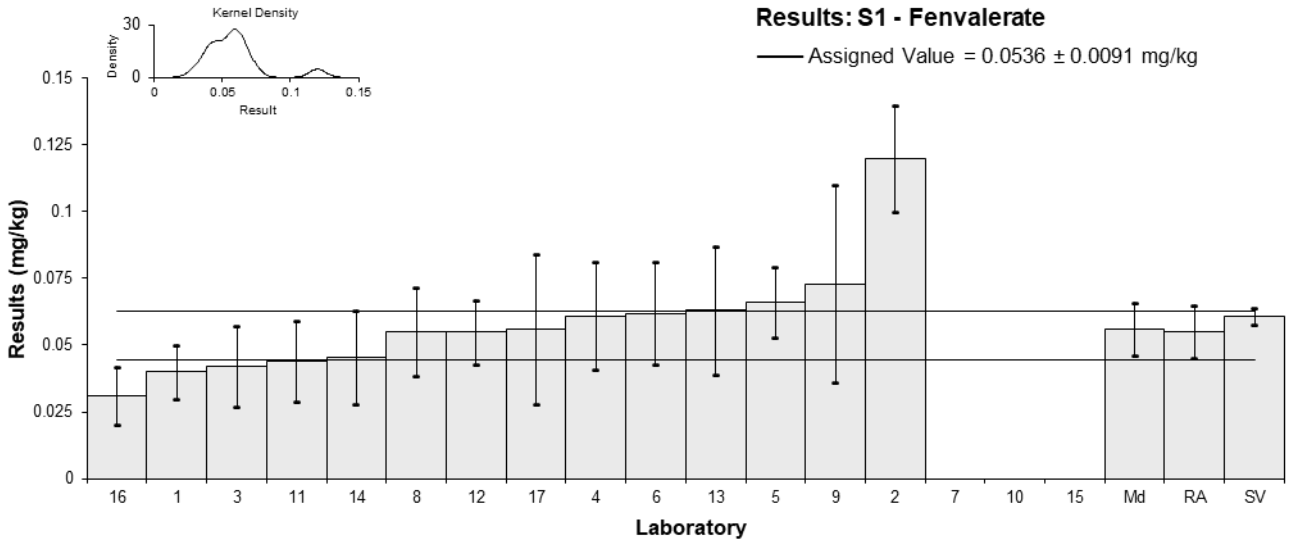
Participant Results

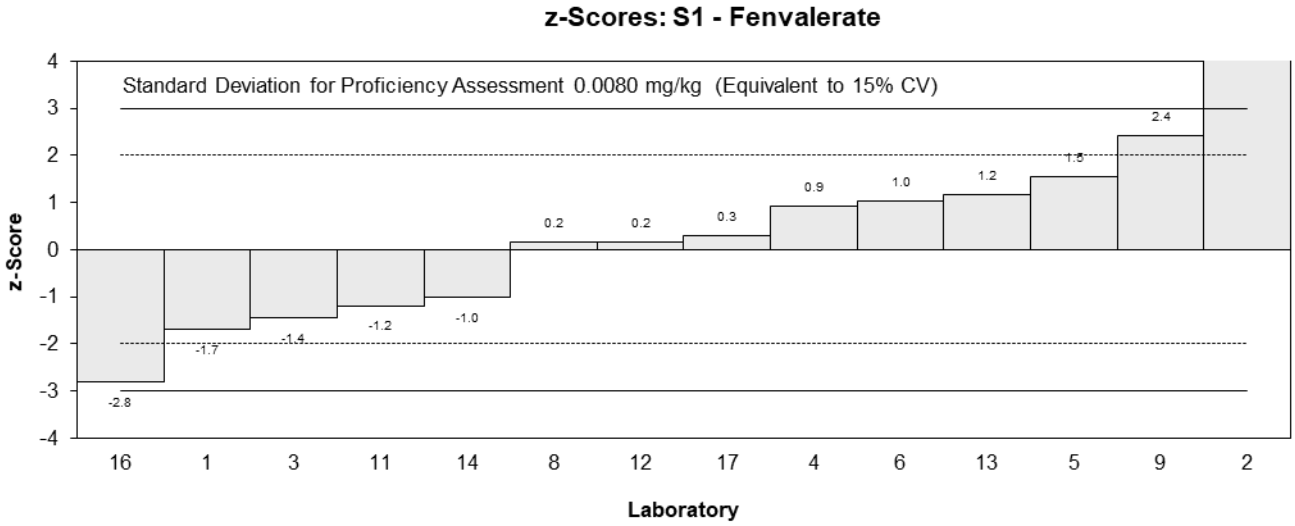
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.04	0.01	122	-1.69	-1.01
2*	0.12	0.02	83	8.26	3.02
3	0.042	0.015	92	-1.44	-0.66
4	0.061	0.02	116	0.92	0.34
5	0.066	0.0132	NR	1.54	0.77
6	0.062	0.019	98	1.04	0.40
7	<0.05	NR	NR		
8	0.055	0.0165	80	0.17	0.07
9	0.073	0.037	126	2.41	0.51
10	< 0.05	NR	NR		
11	0.044	0.015	106	-1.19	-0.55
12	0.055	0.012	88	0.17	0.09
13	0.063	0.024	106	1.17	0.37
14	0.0455	0.0175	100	-1.01	-0.41
15	NS	NS	NS		
16	0.031	0.011	96	-2.81	-1.58
17	0.056	0.028	91	0.30	0.08

* Outlier, see Section 4.2

Statistics

Assigned Value	0.0536	0.0091
Spike Value	0.0607	0.0030
Robust Average	0.0552	0.0098
Median	0.056	0.010
Mean	0.058	
N	14	
Max	0.12	
Min	0.031	
Robust SD	0.015	
Robust CV	27%	


Kernel Density
Density
Result
Results: S1 - Fenvalerate
Assigned Value = 0.0536 ± 0.0091 mg/kg
Results (mg/kg)
Laboratory
16 1 3 11 14 8 12 17 4 6 13 5 9 2 7 10 15 Md RA SV


z-Scores: S1 - Fenvalerate
Standard Deviation for Proficiency Assessment 0.0080 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
16 1 3 11 14 8 12 17 4 6 13 5 9 2
-2.8 -1.7 -1.4 -1.2 -1.0 0.2 0.2 0.3 0.9 1.0 1.2 1.5 2.4

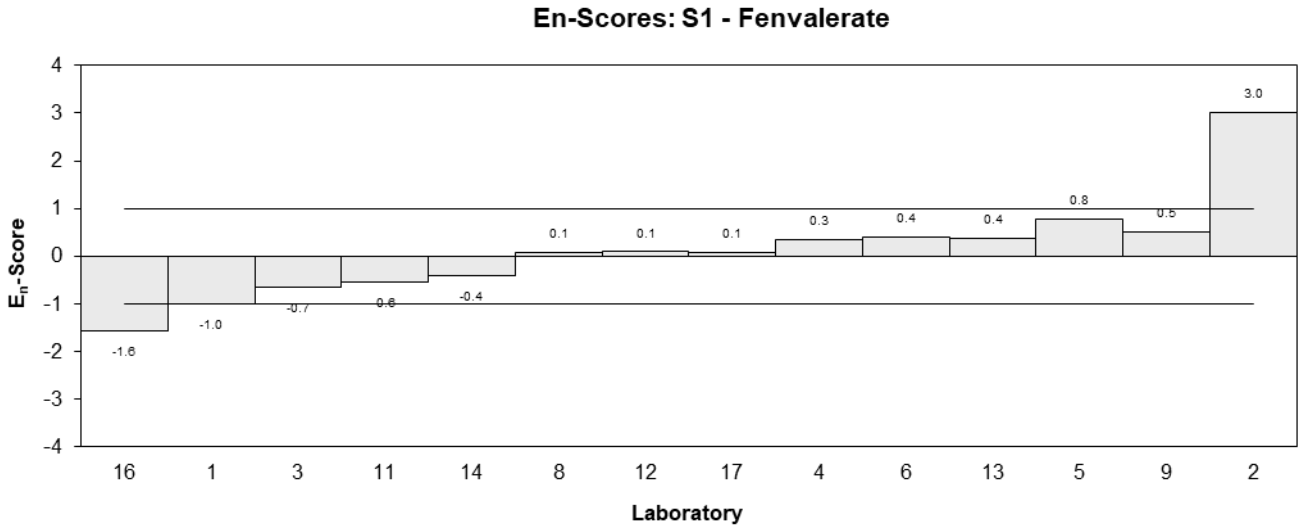

En-Scores: S1 - Fenvalerate
En-Score
Laboratory
16 1 3 11 14 8 12 17 4 6 13 5 9 2
-1.6 -1.0 -0.7 -0.6 -0.4 0.1 0.1 0.1 0.3 0.4 0.4 0.8 0.5 3.0

Figure 6

Table 11

Sample Details

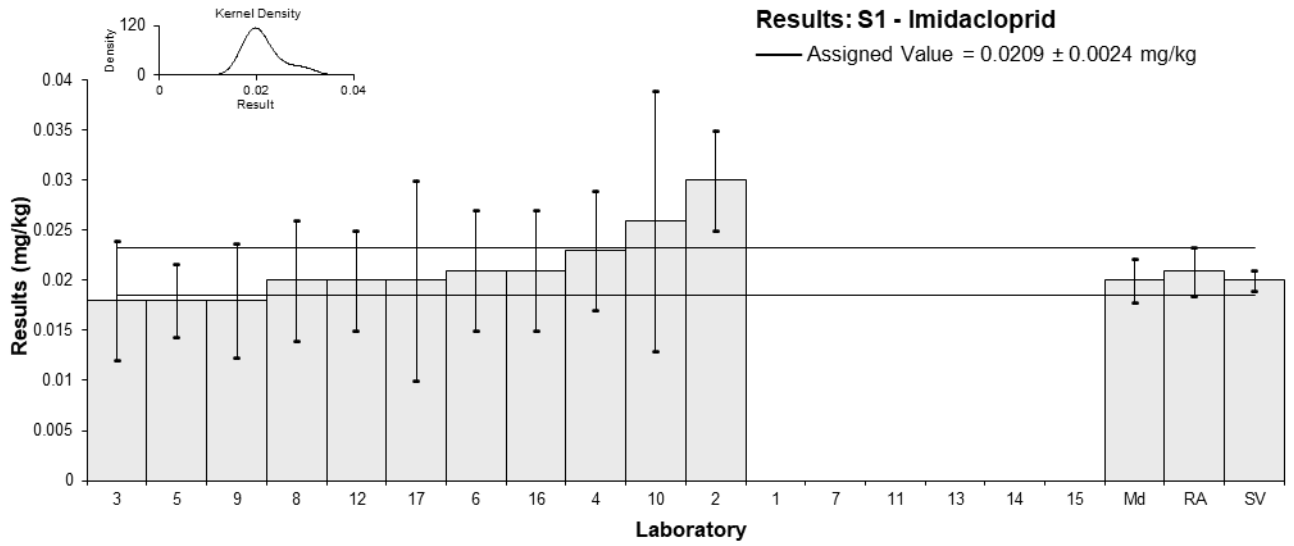
Sample No.	S1
Matrix	Tomato
Analyte	Imidacloprid
Unit	mg/kg

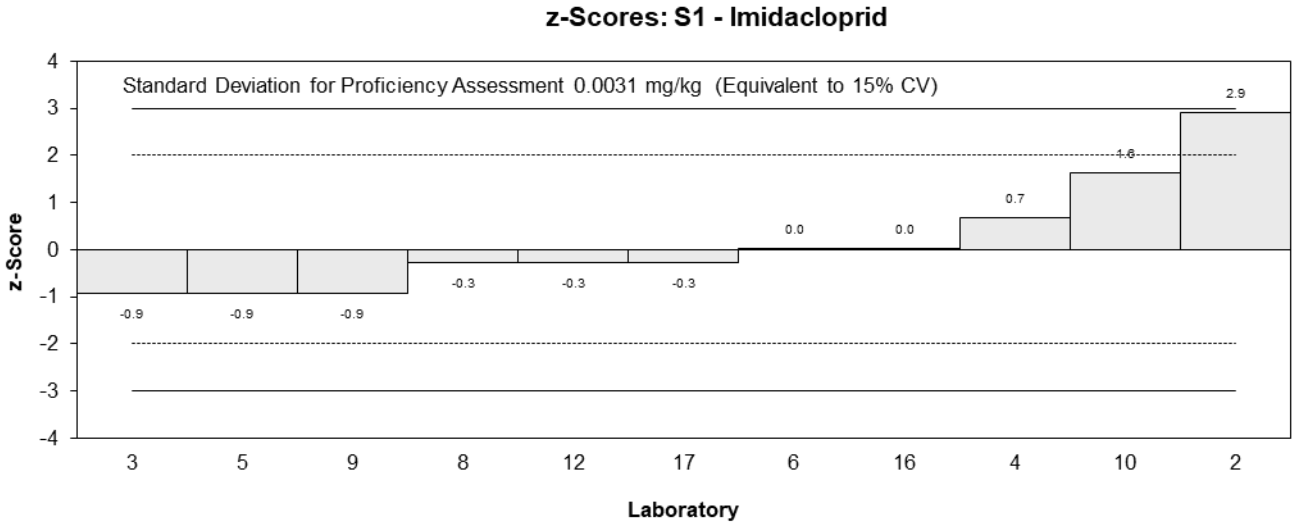
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	NT	NT	NT		
2	0.03	0.005	106	2.90	1.64
3	0.018	0.006	120	-0.93	-0.45
4	0.023	0.006	97	0.67	0.32
5	0.018	0.0036	NR	-0.93	-0.67
6	0.021	0.0060	96	0.03	0.02
7	NT	NT	NT		
8	0.02	0.006	84	-0.29	-0.14
9	0.018	0.0057	75	-0.93	-0.47
10	0.026	0.013	72	1.63	0.39
11	NT	NT	NT		
12	0.020	0.005	100	-0.29	-0.16
13	NT	NT	NT		
14	NT	NT	NT		
15	NS	NS	NS		
16	0.021	0.006	92	0.03	0.02
17	0.020	0.010	80	-0.29	-0.09

Statistics

Assigned Value	0.0209	0.0024
Spike Value	0.0200	0.0010
Robust Average	0.0209	0.0024
Median	0.0200	0.0022
Mean	0.0214	
N	11	
Max	0.03	
Min	0.018	
Robust SD	0.0032	
Robust CV	15%	


Kernel Density
Density
120
0
0
0.02
0.04
Result
Results: S1 - Imidacloprid
Assigned Value = 0.0209 ± 0.0024 mg/kg
Results (mg/kg)
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
3 5 9 8 12 17 6 16 4 10 2 1 7 11 13 14 15 Md RA SV
Laboratory


z-Scores: S1 - Imidacloprid
Standard Deviation for Proficiency Assessment 0.0031 mg/kg (Equivalent to 15% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-0.9 -0.9 -0.9 -0.3 -0.3 -0.3 0.0 0.0 0.7 1.6 2.9
3 5 9 8 12 17 6 16 4 10 2
Laboratory

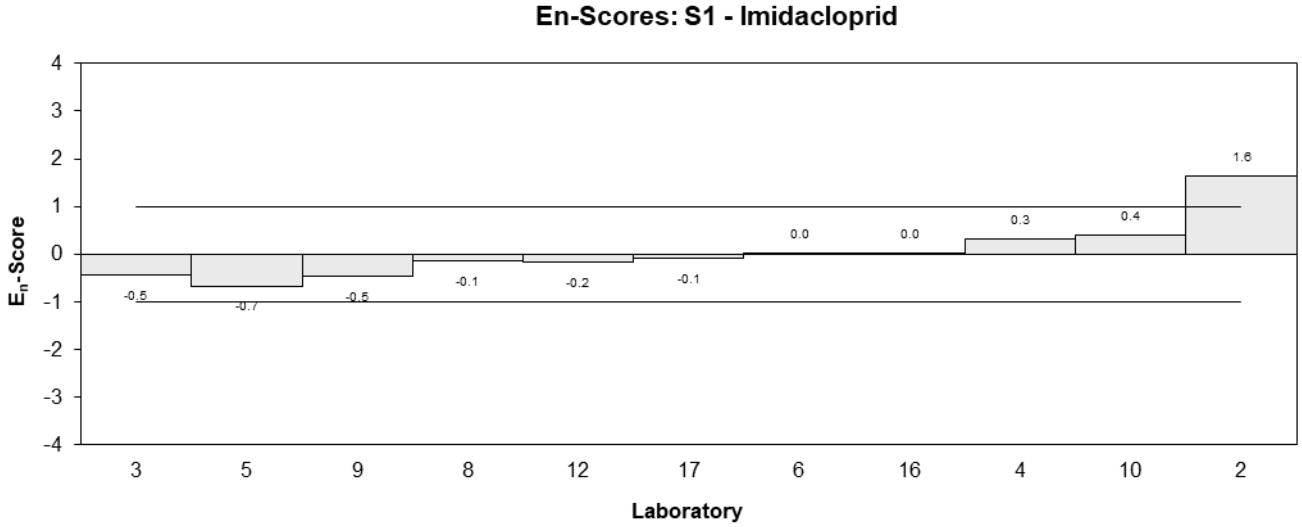

En-Scores: S1 - Imidacloprid
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.5 -0.7 -0.5 -0.1 -0.2 -0.1 0.0 0.0 0.3 0.4 1.6
3 5 9 8 12 17 6 16 4 10 2
Laboratory

Figure 7

Table 12

Sample Details

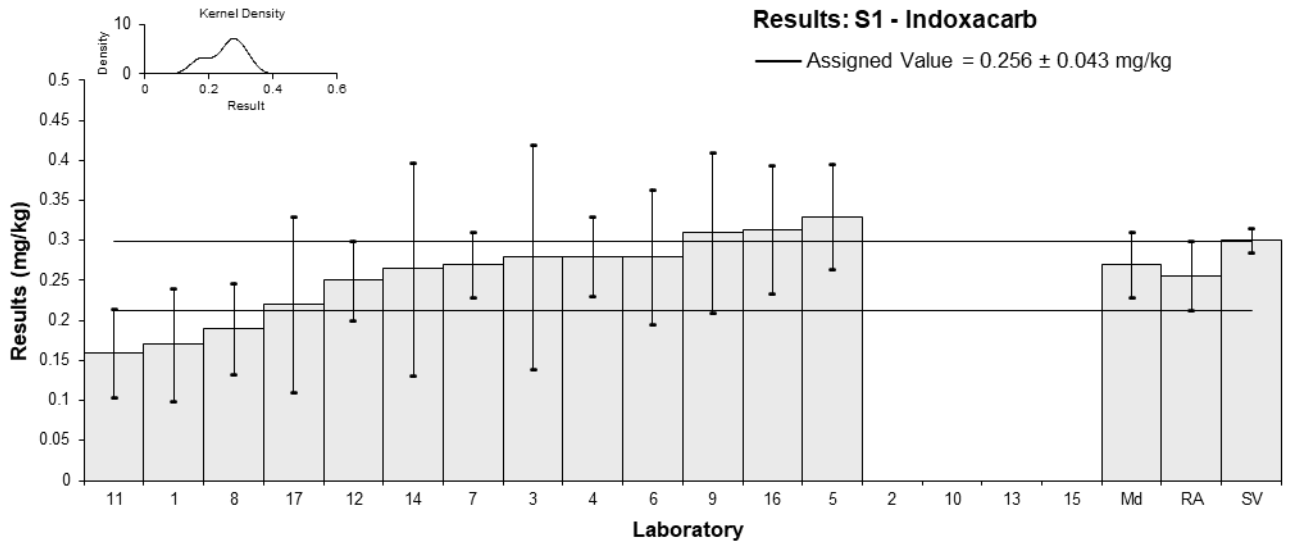
Sample No.	S1
Matrix	Tomato
Analyte	Indoxacarb
Unit	mg/kg

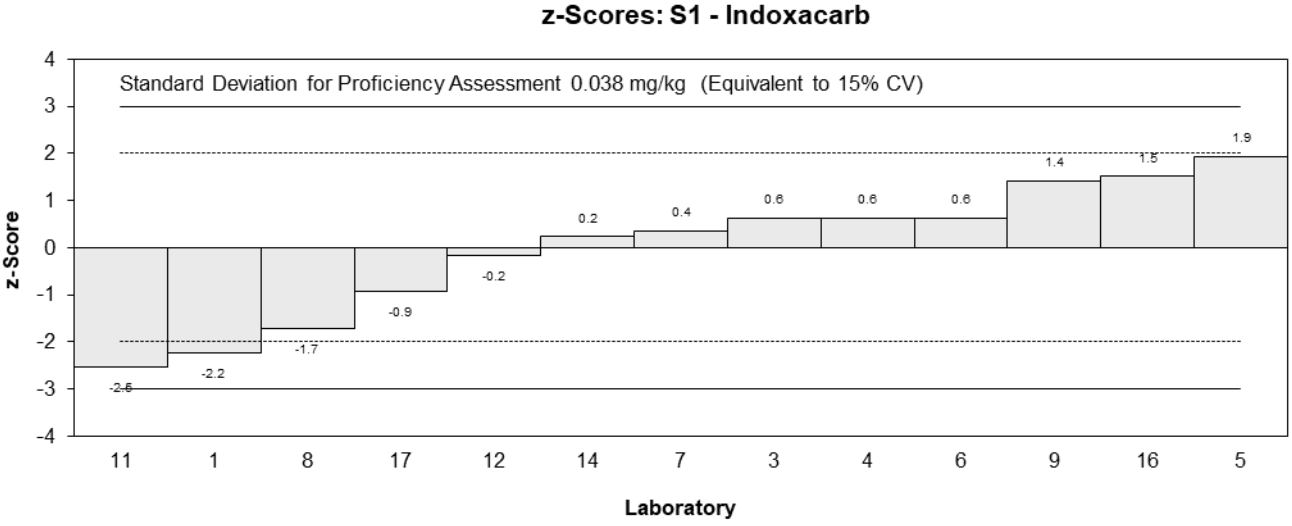
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.17	0.07	89	-2.24	-1.05
2	NT	NT	NT		
3	0.28	0.14	119	0.63	0.16
4	0.28	0.05	99	0.63	0.36
5	0.33	0.066	NR	1.93	0.94
6	0.28	0.084	98	0.63	0.25
7	0.27	0.0405	95.8	0.36	0.24
8	0.19	0.057	79	-1.72	-0.92
9	0.31	0.10	92	1.41	0.50
10	NT	NT	NT		
11	0.159	0.055	111	-2.53	-1.39
12	0.25	0.050	89	-0.16	-0.09
13	NT	NT	NT		
14	0.265	0.133	138	0.23	0.06
15	NS	NS	NS		
16	0.314	0.08	80	1.51	0.64
17	0.22	0.11	113	-0.94	-0.30

Statistics

Assigned Value	0.256	0.043
Spike Value	0.300	0.015
Robust Average	0.256	0.043
Median	0.270	0.041
Mean	0.255	
N	13	
Max	0.33	
Min	0.159	
Robust SD	0.062	
Robust CV	24%	


Kernel Density
Density
Result
Results: S1 - Indoxacarb
Assigned Value = 0.256 ± 0.043 mg/kg
Results (mg/kg)
Laboratory
11 1 8 17 12 14 7 3 4 6 9 16 5 2 10 13 15 Md RA SV


z-Scores: S1 - Indoxacarb
Standard Deviation for Proficiency Assessment 0.038 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
11 1 8 17 12 14 7 3 4 6 9 16 5
-2.6 -2.2 -1.7 -0.9 -0.2 0.2 0.4 0.6 0.6 0.6 1.4 1.5 1.9

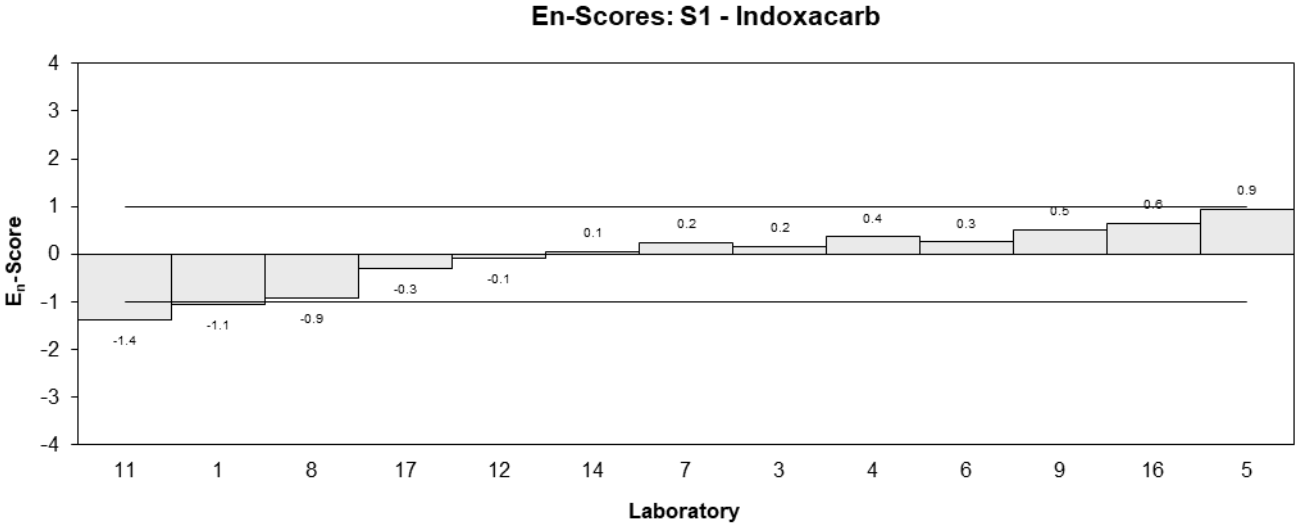

En-Scores: S1 - Indoxacarb
En-Score
Laboratory
11 1 8 17 12 14 7 3 4 6 9 16 5
-1.4 -1.1 -0.9 -0.3 -0.1 0.1 0.2 0.2 0.4 0.3 0.5 0.6 0.9

Figure 8

Table 13

Sample Details

Sample No.	S1
Matrix	Tomato
Analyte	Methomyl
Unit	mg/kg

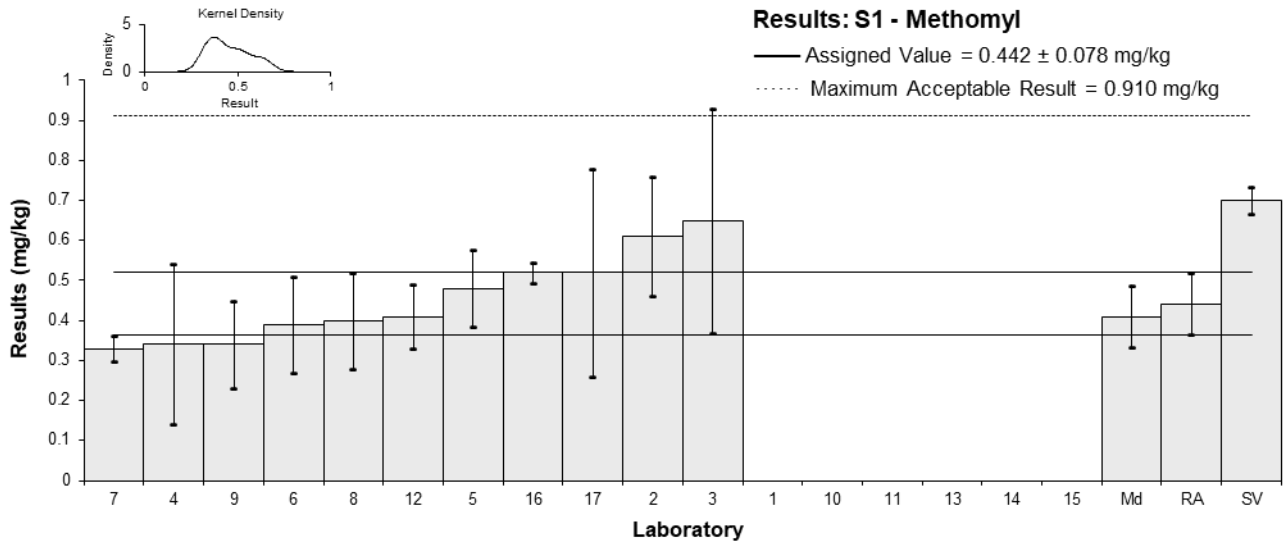
Participant Results

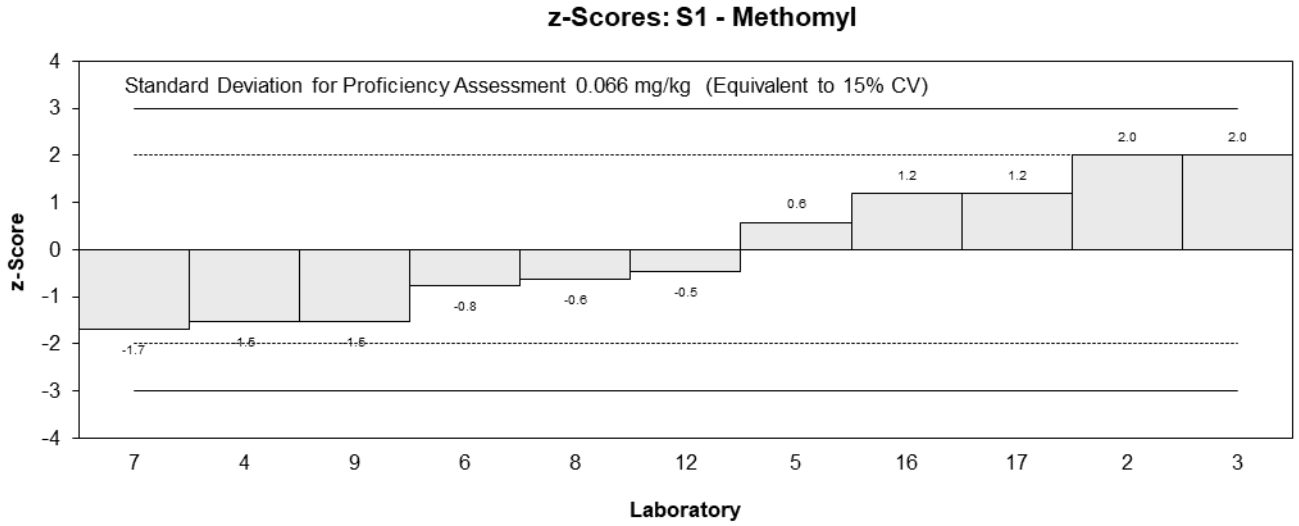
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	NT	NT	NT		
2	0.61	0.15	84	2.00▼	
3	0.65	0.28	119	2.00▼	
4	0.34	0.2	95	-1.54	-0.48
5	0.48	0.096	NR	0.57	0.31
6	0.39	0.12	98	-0.78	-0.36
7	0.33	0.033	85.05	-1.69	-1.32
8	0.40	0.12	87	-0.63	-0.29
9	0.34	0.11	74	-1.54	-0.76
10	NT	NT	NT		
11	NT	NT	NT		
12	0.41	0.080	92	-0.48	-0.29
13	NT	NT	NT		
14	NT	NT	NT		
15	NS	NS	NS		
16	0.52	0.026	77	1.18	0.95
17	0.52	0.26	90	1.18	0.29

▼ Adjusted Score, see Section 6.3

Statistics

Assigned Value	0.442	0.078
Spike Value	0.700	0.035
Robust Average	0.442	0.078
Max Acceptable Result	0.910	
Median	0.410	0.078
Mean	0.454	
N	11	
Max	0.65	
Min	0.33	
Robust SD	0.10	
Robust CV	23%	


Kernel Density
Density
Result
Results: S1 - Methomyl
Assigned Value = 0.442 ± 0.078 mg/kg
Maximum Acceptable Result = 0.910 mg/kg
Results (mg/kg)
Laboratory
7 4 9 6 8 12 5 16 17 2 3 1 10 11 13 14 15 Md RA SV


z-Scores: S1 - Methomyl
Standard Deviation for Proficiency Assessment 0.066 mg/kg (Equivalent to 15% CV)
z-Score
-1.7 -1.6 -1.5 -0.8 -0.6 -0.5 0.6 1.2 1.2 2.0 2.0
Laboratory
7 4 9 6 8 12 5 16 17 2 3

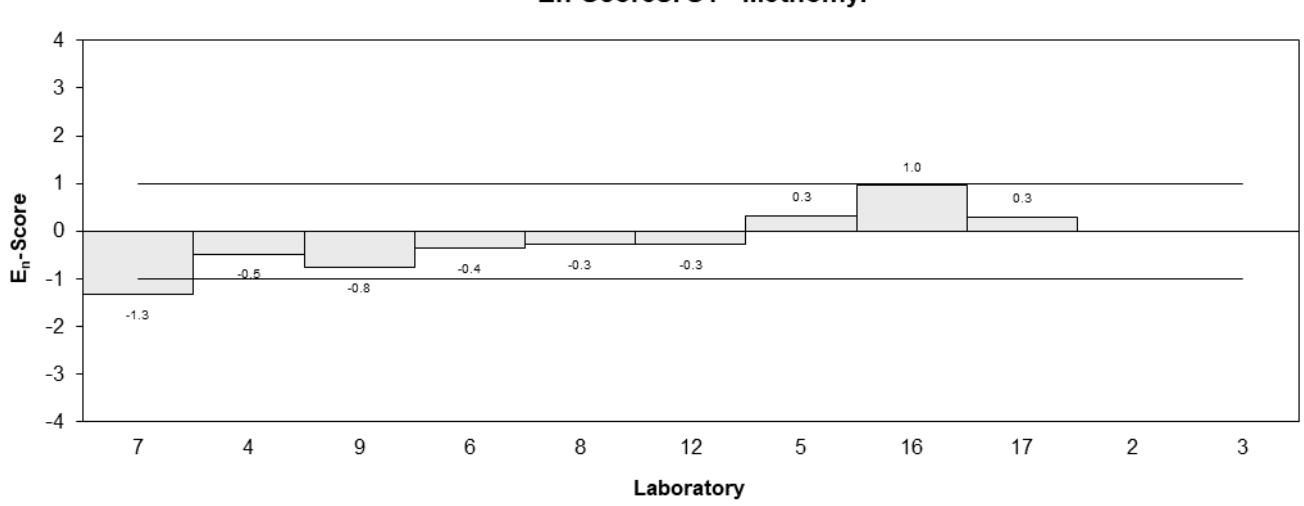

En-Scores: S1 - Methomyl
En-Score
-1.3 -0.5 -0.8 -0.4 -0.3 -0.3 0.3 1.0 0.3
Laboratory
7 4 9 6 8 12 5 16 17 2 3

Figure 9

Table 14

Sample Details

Sample No.	S2
Matrix	Blueberry
Analyte	Bifenthrin
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	0.01	0.005	129
2	0.02	0.003	89
3	0.014	0.007	254
4	0.023	0.006	101
5	0.0098	0.00196	NR
6	0.020	0.0060	105
7	0.01	0.02	95.19
8	<0.01	NR	NR
9	0.026	0.011	99
10	0.02	0.01	127
11	NR	NR	110
12	0.019	0.003	104
13	0.016	0.0032	99
14	0.0107	0.00460	82
15	NS	NS	NS
16	0.021	0.004	81
17	NS	NS	NS

Statistics

Assigned Value	Not Set	
Spike Value	Not Spiked	
Robust Average	0.0169	0.0043
Median	0.0190	0.0041
Mean	0.0169	
N	13	
Max	0.026	
Min	0.0098	
Robust SD	0.0062	
Robust CV	37%	

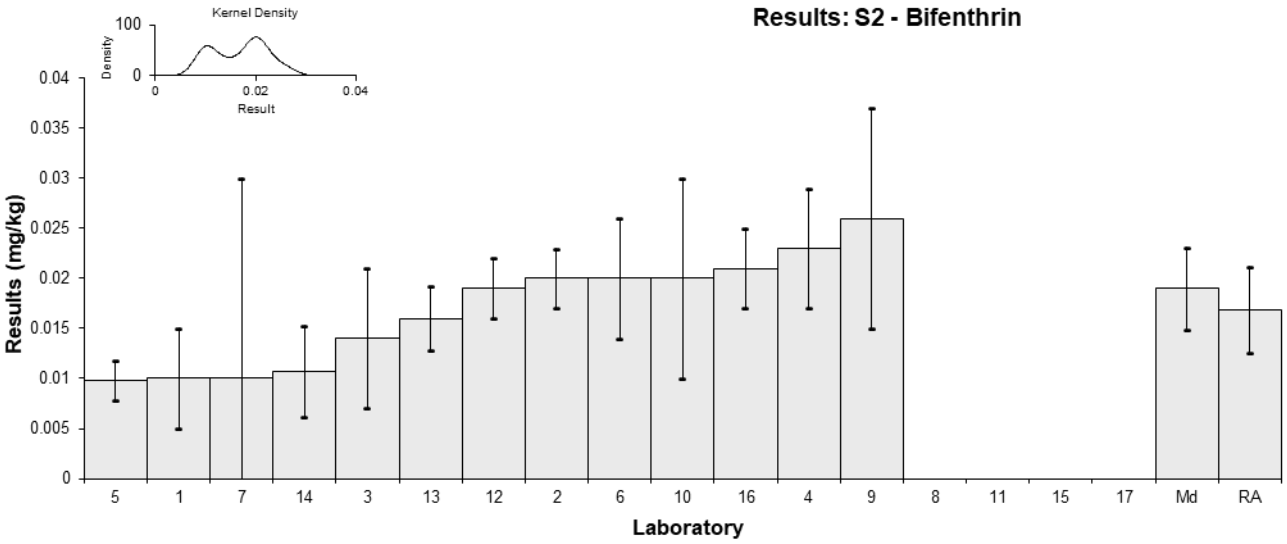

Kernel Density
100
Density
0
0
0.02
0.04
Result
Results: S2 - Bifenthrin
Results (mg/kg)
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
5
1
7
14
3
13
12
2
6
10
16
4
9
8
11
15
17
Md
RA
Laboratory

Figure 10

Table 15

Sample Details

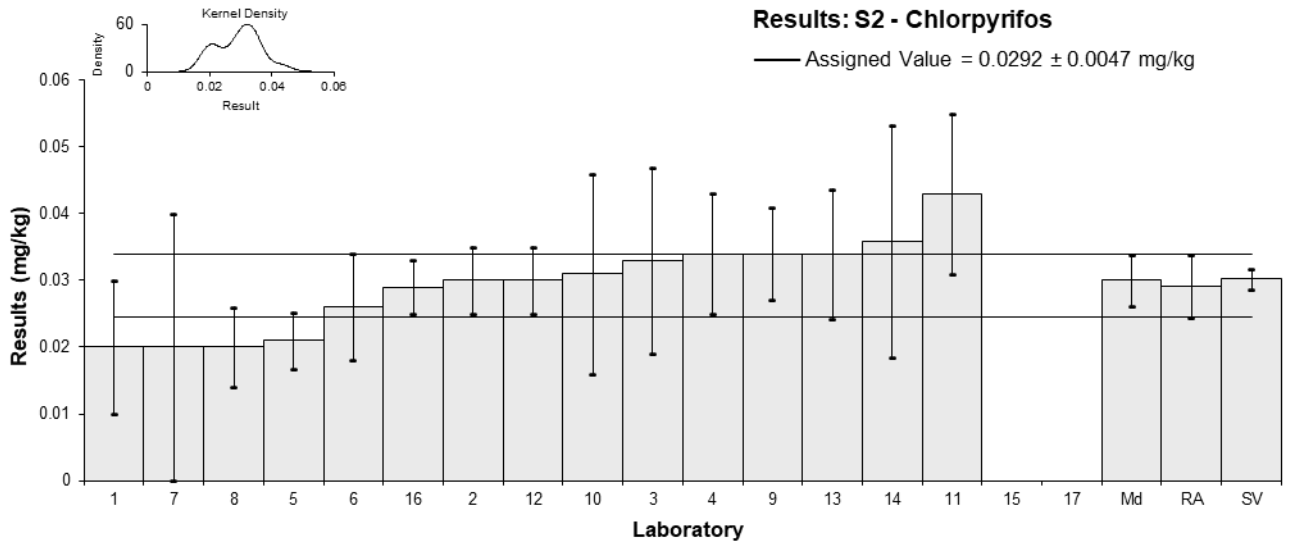
Sample No.	S2
Matrix	Blueberry
Analyte	Chlorpyrifos
Unit	mg/kg

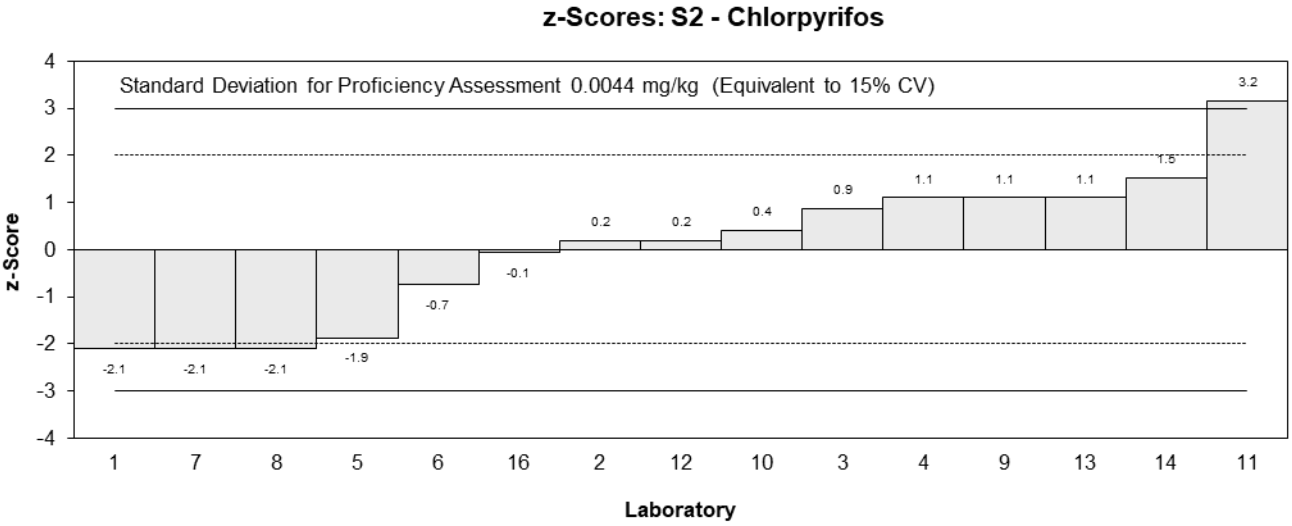
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.02	0.01	105	-2.10	-0.83
2	0.03	0.005	92	0.18	0.12
3	0.033	0.014	72	0.87	0.26
4	0.034	0.009	92	1.10	0.47
5	0.021	0.0042	NR	-1.87	-1.30
6	0.026	0.0080	110	-0.73	-0.34
7	0.02	0.02	83.34	-2.10	-0.45
8	0.02	0.006	79	-2.10	-1.21
9	0.034	0.0069	106	1.10	0.57
10	0.031	0.015	85	0.41	0.11
11	0.043	0.012	107	3.15	1.07
12	0.030	0.005	94	0.18	0.12
13	0.034	0.0097	97	1.10	0.45
14	0.0359	0.0174	133	1.53	0.37
15	NS	NS	NS		
16	0.029	0.004	86	-0.05	-0.03
17	NS	NS	NS		

Statistics

Assigned Value	0.0292	0.0047
Spike Value	0.0302	0.0015
Robust Average	0.0292	0.0047
Median	0.0300	0.0038
Mean	0.0294	
N	15	
Max	0.043	
Min	0.02	
Robust SD	0.0073	
Robust CV	25%	


Kernel Density
Density
Result
Results: S2 - Chlorpyrifos
Assigned Value = 0.0292 ± 0.0047 mg/kg
Results (mg/kg)
Laboratory
1 7 8 5 6 16 2 12 10 3 4 9 13 14 11 15 17 Md RA SV


z-Scores: S2 - Chlorpyrifos
Standard Deviation for Proficiency Assessment 0.0044 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
1 7 8 5 6 16 2 12 10 3 4 9 13 14 11
-2.1 -2.1 -2.1 -1.9 -0.7 -0.1 0.2 0.2 0.4 0.9 1.1 1.1 1.1 1.5 3.2

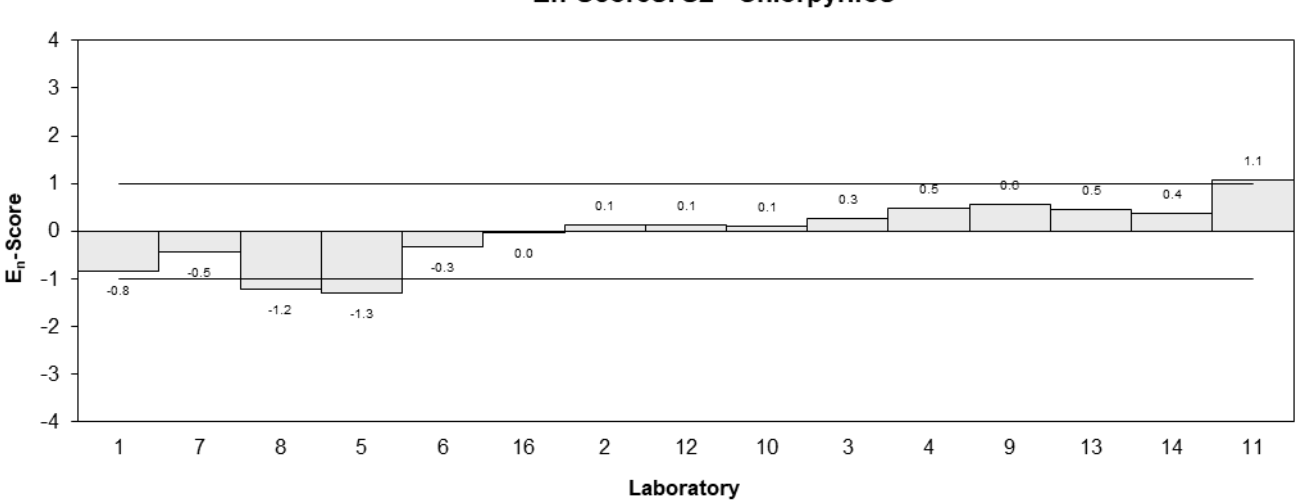

En-Scores: S2 - Chlorpyrifos
En-Score
Laboratory
1 7 8 5 6 16 2 12 10 3 4 9 13 14 11
-0.8 -0.5 -1.2 -1.3 -0.3 0.0 0.1 0.1 0.1 0.3 0.5 0.6 0.5 0.4 1.1

Figure 11

Table 16

Sample Details

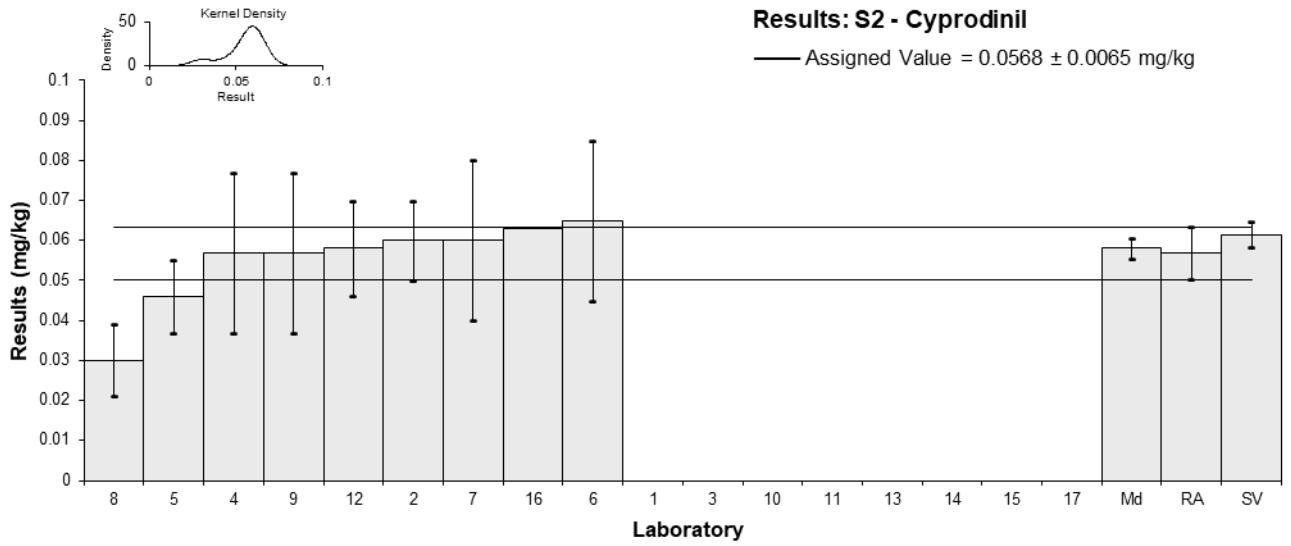
Sample No.	S2
Matrix	Blueberry
Analyte	Cyprodinil
Unit	mg/kg

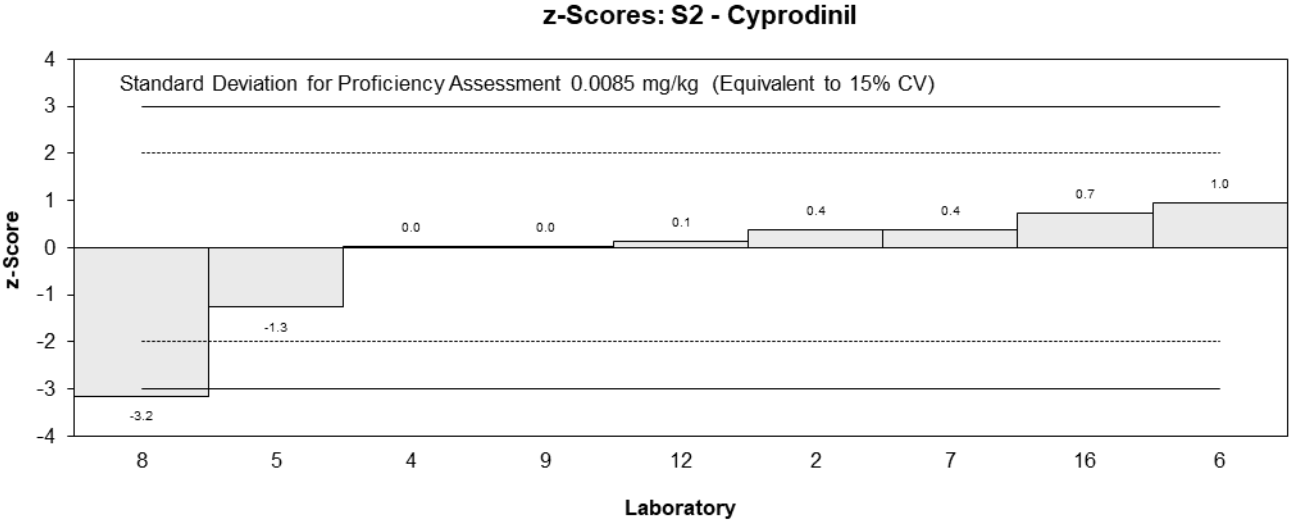
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	NT	NT	NT		
2	0.06	0.01	132	0.38	0.27
3	NT	NT	NT		
4	0.057	0.02	92	0.02	0.01
5	0.046	0.0092	NR	-1.27	-0.96
6	0.065	0.02	95	0.96	0.39
7	0.06	0.02	105.56	0.38	0.15
8	0.03	0.009	76	-3.15	-2.41
9	0.057	0.020	130	0.02	0.01
10	NT	NT	NT		
11	NT	NT	NT		
12	0.058	0.012	92	0.14	0.09
13	NT	NT	NT		
14	NT	NT	NT		
15	NS	NS	NS		
16	0.063	NR	94	0.73	0.95
17	NS	NS	NS		

Statistics

Assigned Value	0.0568	0.0065
Spike Value	0.0615	0.0031
Robust Average	0.0568	0.0065
Median	0.0580	0.0025
Mean	0.0551	
N	9	
Max	0.065	
Min	0.03	
Robust SD	0.0078	
Robust CV	14%	


Kernel Density
Density
Result
Results: S2 - Cyprodinil
Assigned Value = 0.0568 ± 0.0065 mg/kg
Results (mg/kg)
Laboratory
8 5 4 9 12 2 7 16 6 1 3 10 11 13 14 15 17 Md RA SV


z-Scores: S2 - Cyprodinil
Standard Deviation for Proficiency Assessment 0.0085 mg/kg (Equivalent to 15% CV)
z-Score
-3.2
-1.3
0.0
0.0
0.1
0.4
0.4
0.7
1.0
Laboratory
8 5 4 9 12 2 7 16 6

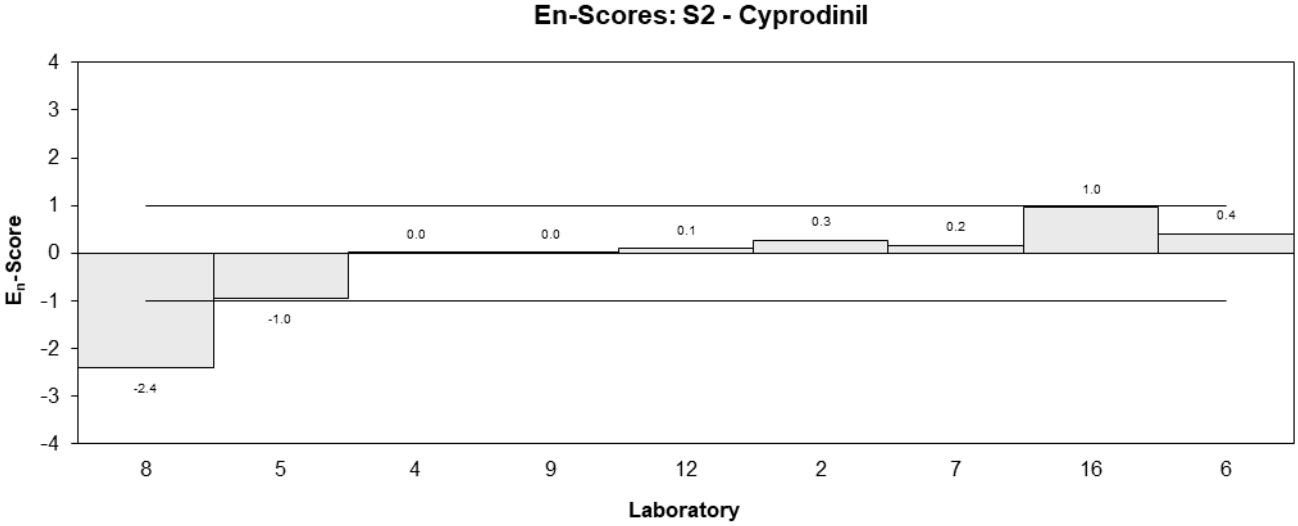

En-Scores: S2 - Cyprodinil
En-Score
-2.4
-1.0
0.0
0.0
0.1
0.3
0.2
1.0
0.4
Laboratory
8 5 4 9 12 2 7 16 6

Figure 12

Table 17

Sample Details

Sample No.	S2
Matrix	Blueberry
Analyte	Dimethoate
Unit	mg/kg

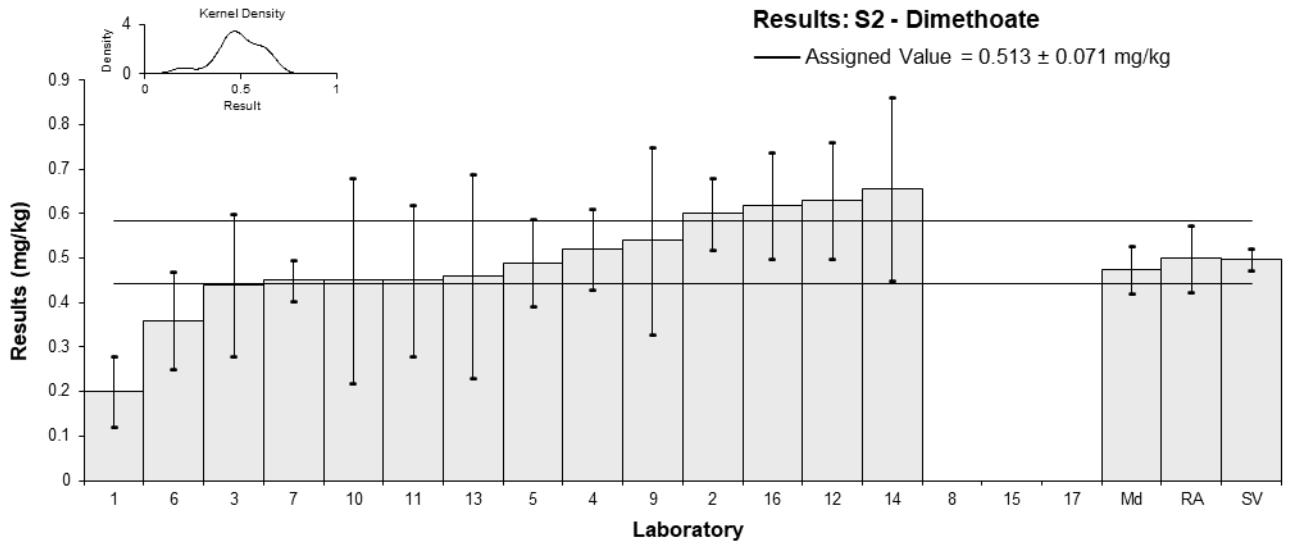
Participant Results

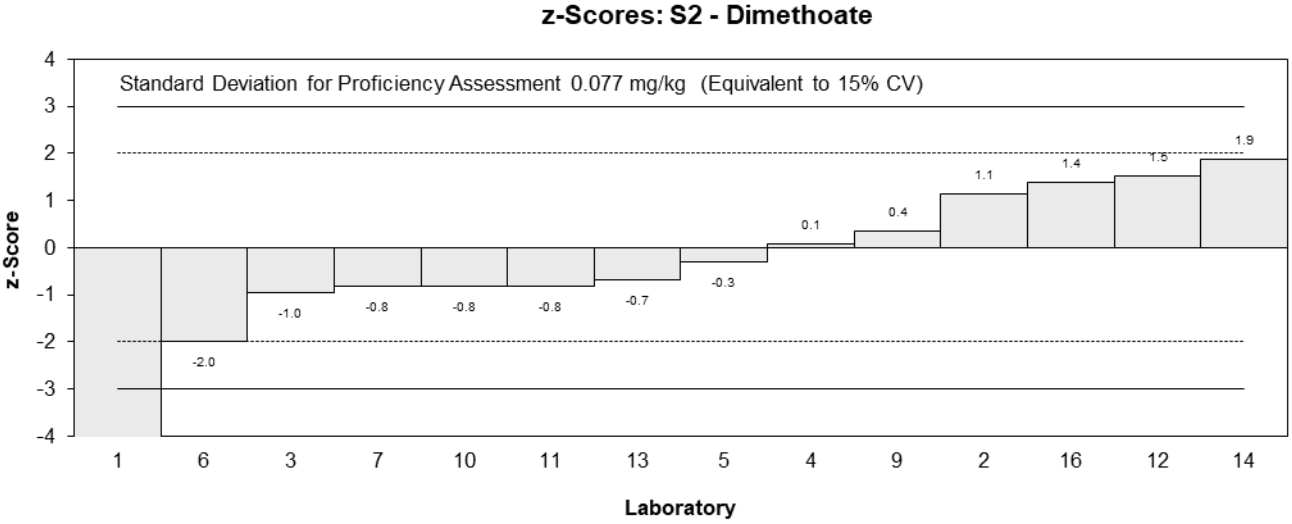
Lab. Code	Result	Uncertainty	Rec	z	E_n
1*	0.2	0.08	96	-4.07	-2.93
2	0.6	0.08	102	1.13	0.81
3	0.44	0.16	72	-0.95	-0.42
4	0.52	0.09	94	0.09	0.06
5	0.49	0.098	NR	-0.30	-0.19
6	0.36	0.11	109	-1.99	-1.17
7	0.45	0.045	84.11	-0.82	-0.75
8	<0.01	NR	NR		
9	0.54	0.210	93	0.35	0.12
10	0.45	0.23	76	-0.82	-0.26
11	0.45	0.17	101	-0.82	-0.34
12	0.63	0.13	114	1.52	0.79
13	0.46	0.23	132	-0.69	-0.22
14	0.657	0.206	130	1.87	0.66
15	NS	NS	NS		
16	0.619	0.12	70	1.38	0.76
17	NS	NS	NS		

* Outlier, see Section 4.2

Statistics

Assigned Value	0.513	0.071
Spike Value	0.497	0.025
Robust Average	0.500	0.075
Median	0.475	0.054
Mean	0.490	
N	14	
Max	0.657	
Min	0.2	
Robust SD	0.11	
Robust CV	23%	


Kernel Density
Density
Result
Results: S2 - Dimethoate
Assigned Value = 0.513 ± 0.071 mg/kg
Results (mg/kg)
Laboratory
1 6 3 7 10 11 13 5 4 9 2 16 12 14 8 15 17 Md RA SV


z-Scores: S2 - Dimethoate
Standard Deviation for Proficiency Assessment 0.077 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
1 6 3 7 10 11 13 5 4 9 2 16 12 14
-2.9 -2.0 -1.0 -0.8 -0.8 -0.8 -0.7 -0.3 0.1 0.4 1.1 1.4 1.5 1.9

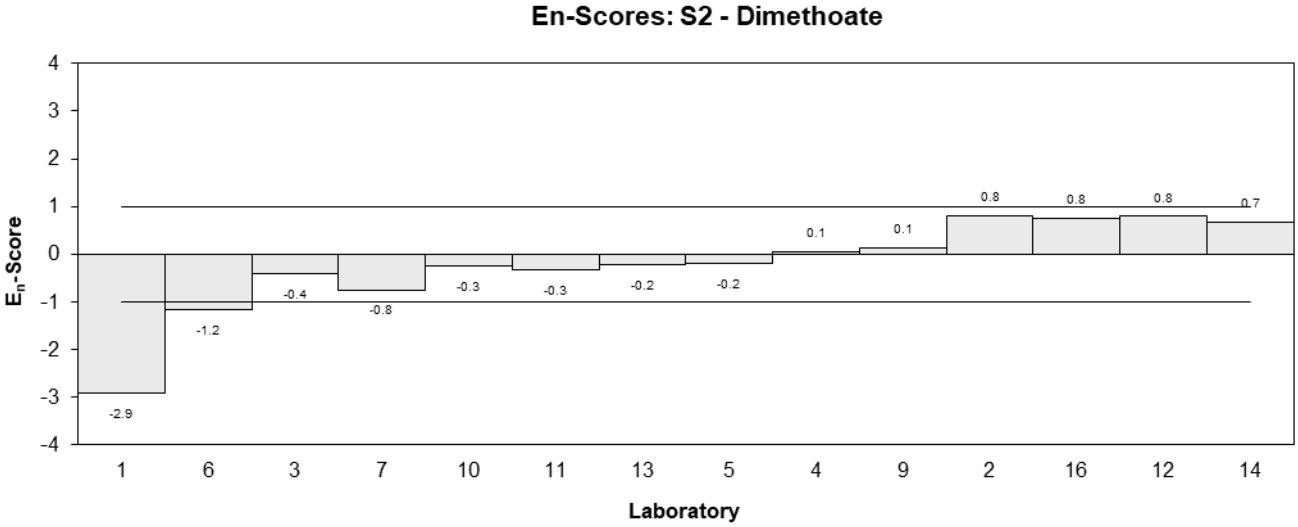

En-Scores: S2 - Dimethoate
En-Score
Laboratory
1 6 3 7 10 11 13 5 4 9 2 16 12 14
-2.9 -1.2 -0.4 -0.8 -0.3 -0.3 -0.2 -0.2 0.1 0.1 0.8 0.8 0.8 0.7

Figure 13

Table 18

Sample Details

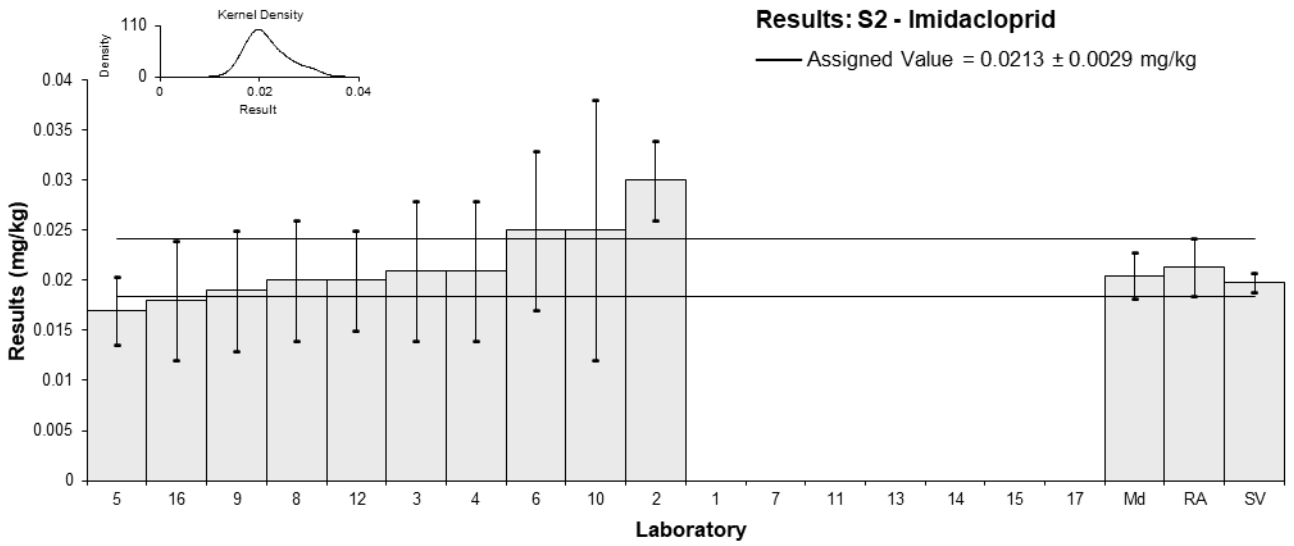
Sample No.	S2
Matrix	Blueberry
Analyte	Imidacloprid
Unit	mg/kg

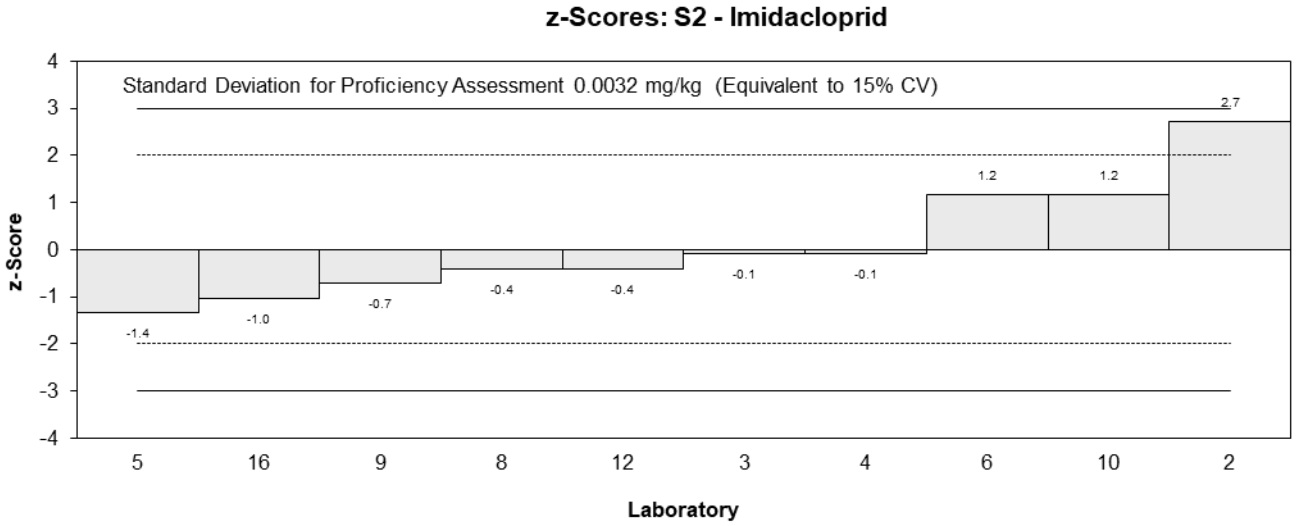
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	NT	NT	NT		
2	0.03	0.004	106	2.72	1.76
3	0.021	0.007	116	-0.09	-0.04
4	0.021	0.007	101	-0.09	-0.04
5	0.017	0.0034	NR	-1.35	-0.96
6	0.025	0.008	97	1.16	0.43
7	NT	NT	NT		
8	0.02	0.006	71	-0.41	-0.20
9	0.019	0.0060	75	-0.72	-0.35
10	0.025	0.013	76	1.16	0.28
11	NT	NT	NT		
12	0.020	0.005	112	-0.41	-0.22
13	NT	NT	NT		
14	NT	NT	NT		
15	NS	NS	NS		
16	0.018	0.006	102	-1.03	-0.50
17	NS	NS	NS		

Statistics

Assigned Value	0.0213	0.0029
Spike Value	0.0198	0.0010
Robust Average	0.0213	0.0029
Median	0.0205	0.0023
Mean	0.0216	
N	10	
Max	0.03	
Min	0.017	
Robust SD	0.0037	
Robust CV	17%	


Kernel Density
Density
110
0
0
0.02
0.04
Result
Results: S2 - Imidacloprid
Assigned Value = 0.0213 ± 0.0029 mg/kg
Results (mg/kg)
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
5
16
9
8
12
3
4
6
10
2
1
7
11
13
14
15
17
Md
RA
SV
Laboratory


z-Scores: S2 - Imidacloprid
Standard Deviation for Proficiency Assessment 0.0032 mg/kg (Equivalent to 15% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.4
-1.0
-0.7
-0.4
-0.4
-0.1
-0.1
1.2
1.2
2.7
5
16
9
8
12
3
4
6
10
2
Laboratory

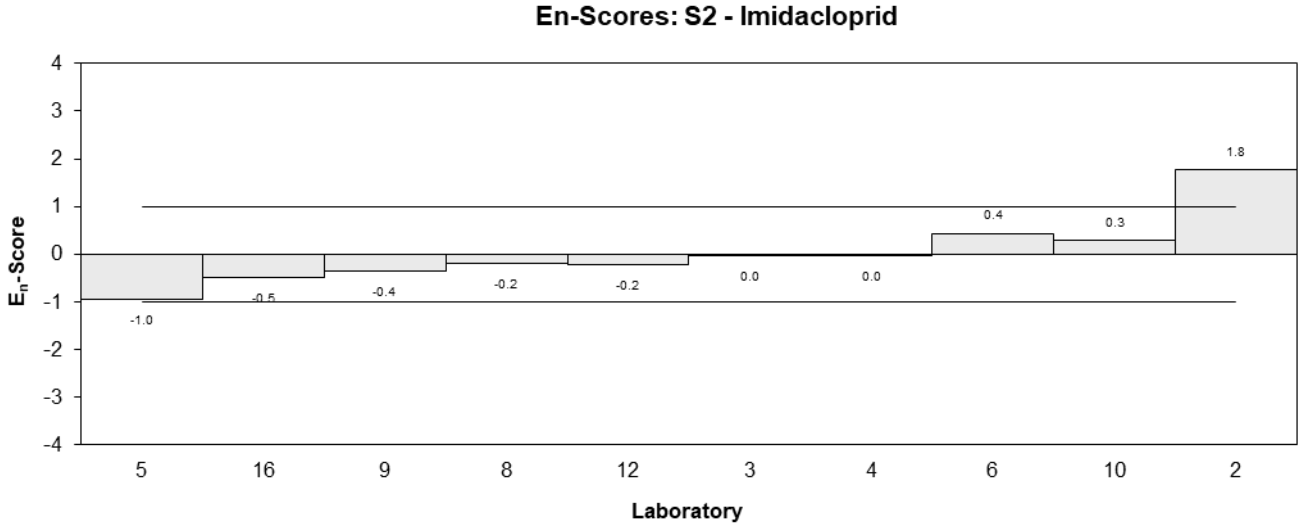

En-Scores: S2 - Imidacloprid
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.0
-0.5
-0.4
-0.2
-0.2
0.0
0.0
0.4
0.3
1.8
5
16
9
8
12
3
4
6
10
2
Laboratory

Figure 14

Table 19

Sample Details

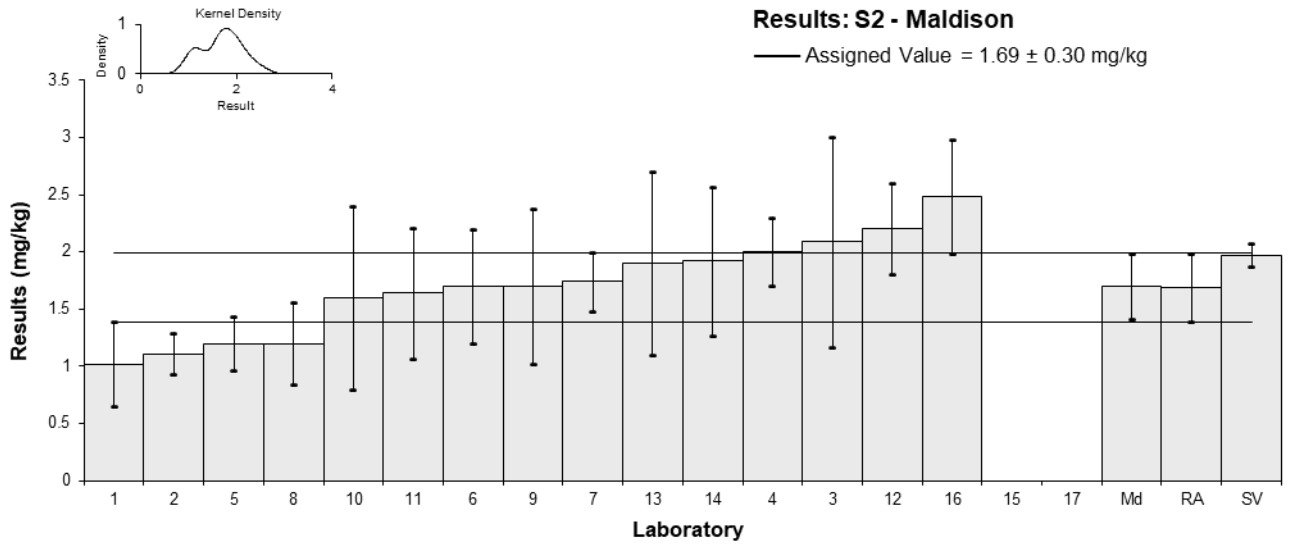
Sample No.	S2
Matrix	Blueberry
Analyte	Maldison
Unit	mg/kg

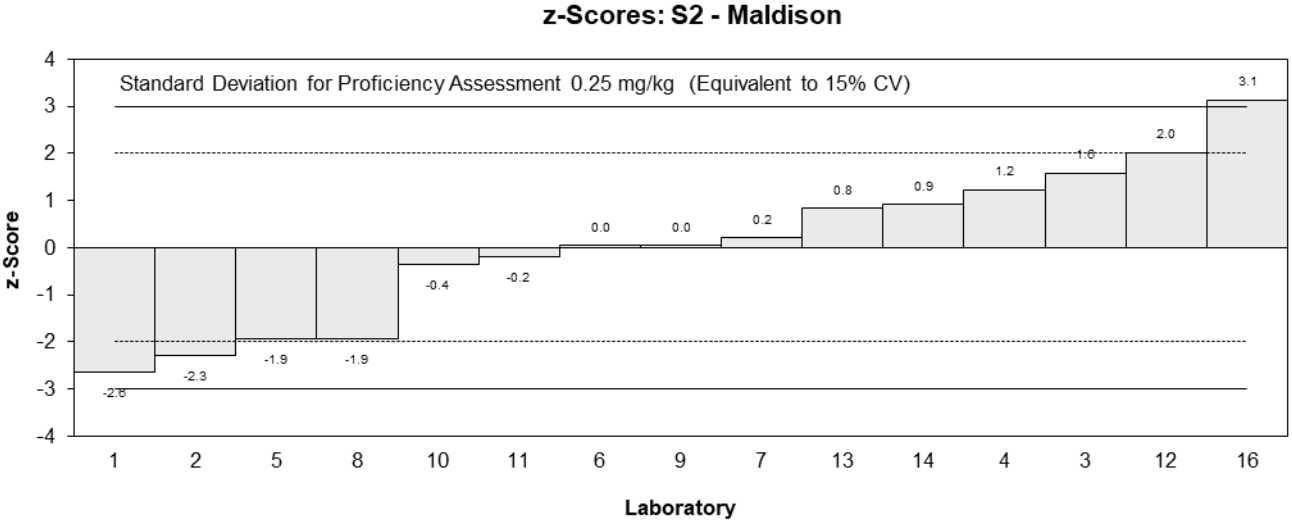
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	1.02	0.37	129	-2.64	-1.41
2	1.11	0.18	90	-2.29	-1.66
3	2.09	0.92	111	1.58	0.41
4	2.0	0.3	97	1.22	0.73
5	1.2	0.24	NR	-1.93	-1.28
6	1.7	0.5	108	0.04	0.02
7	1.74	0.261	108.82	0.20	0.13
8	1.2	0.36	71	-1.93	-1.05
9	1.7	0.68	99	0.04	0.01
10	1.6	0.8	112	-0.36	-0.11
11	1.64	0.57	104	-0.20	-0.08
12	2.20	0.40	94	2.01	1.02
13	1.9	0.80	116	0.83	0.25
14	1.92	0.65	103	0.91	0.32
15	NS	NS	NS		
16	2.48	0.5	88	3.12	1.35
17	NS	NS	NS		

Statistics

Assigned Value	1.69	0.30
Spike Value	1.97	0.10
Robust Average	1.69	0.30
Median	1.70	0.29
Mean	1.70	
N	15	
Max	2.48	
Min	1.02	
Robust SD	0.47	
Robust CV	28%	


Kernel Density
Density
Result
Results: S2 - Maldison
Assigned Value = 1.69 ± 0.30 mg/kg
Results (mg/kg)
Laboratory
1 2 5 8 10 11 6 9 7 13 14 4 3 12 16 15 17 Md RA SV


z-Scores: S2 - Maldison
Standard Deviation for Proficiency Assessment 0.25 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
1 2 5 8 10 11 6 9 7 13 14 4 3 12 16
-2.6 -2.3 -1.9 -1.9 -0.4 -0.2 0.0 0.0 0.2 0.8 0.9 1.2 1.6 2.0 3.1

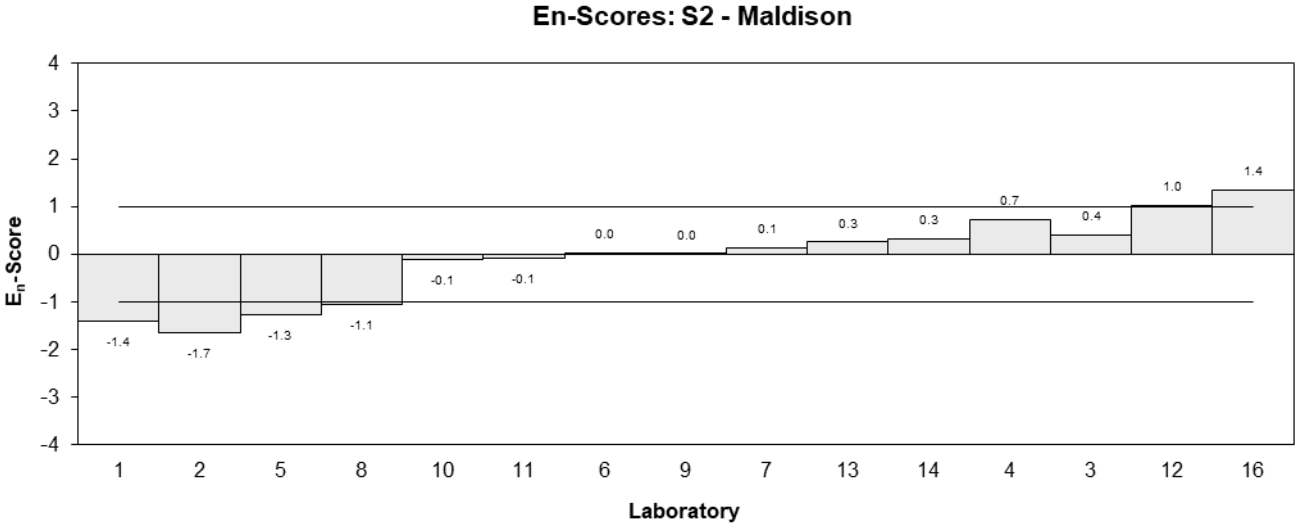

En-Scores: S2 - Maldison
En-Score
Laboratory
1 2 5 8 10 11 6 9 7 13 14 4 3 12 16
-1.4 -1.7 -1.3 -1.1 -0.1 -0.1 0.0 0.0 0.1 0.3 0.3 0.7 0.4 1.0 1.4

Figure 15

Table 20

Sample Details

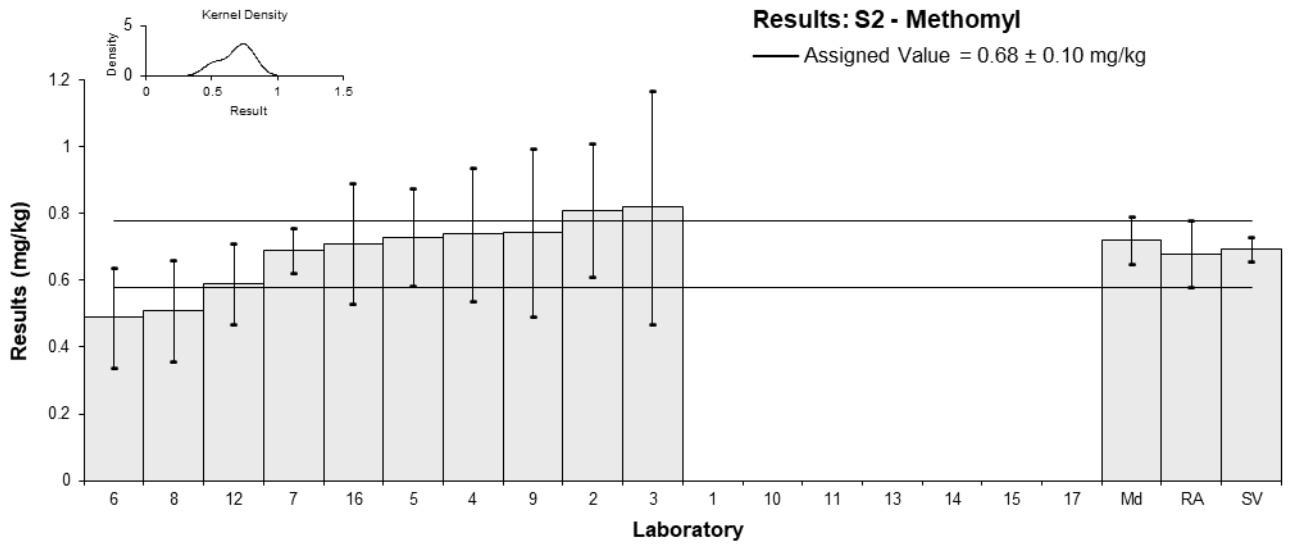
Sample No.	S2
Matrix	Blueberry
Analyte	Methomyl
Unit	mg/kg

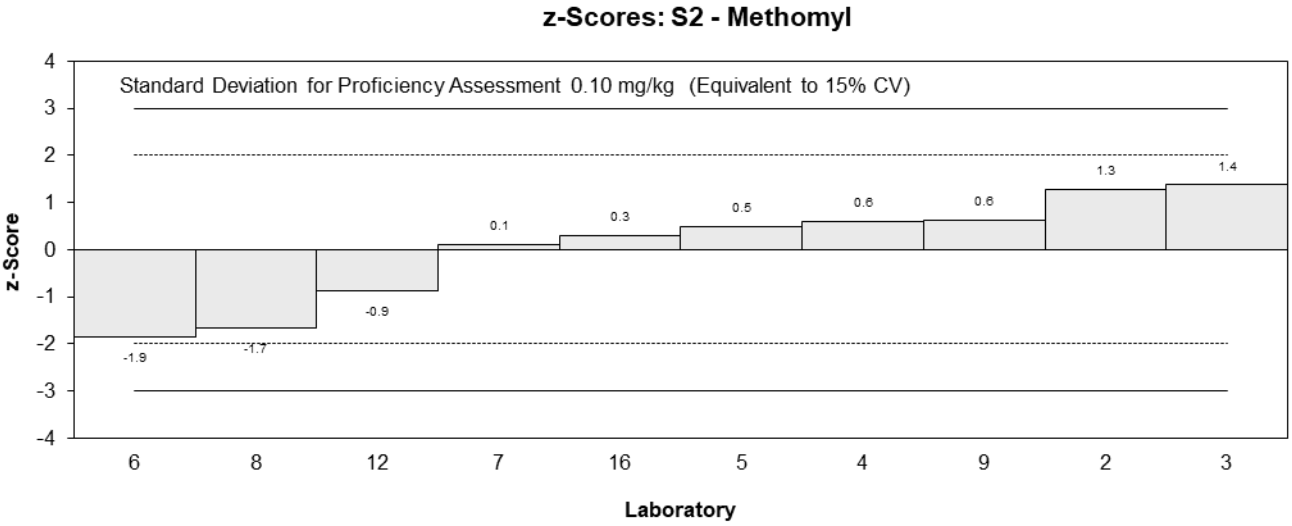
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	NT	NT	NT		
2	0.81	0.2	84	1.27	0.58
3	0.82	0.35	119	1.37	0.38
4	0.74	0.2	87	0.59	0.27
5	0.73	0.146	NR	0.49	0.28
6	0.49	0.15	100	-1.86	-1.05
7	0.69	0.069	85.05	0.10	0.08
8	0.51	0.153	78	-1.67	-0.93
9	0.744	0.25	106	0.63	0.24
10	NT	NT	NT		
11	NT	NT	NT		
12	0.59	0.12	108	-0.88	-0.58
13	NT	NT	NT		
14	NT	NT	NT		
15	NS	NS	NS		
16	0.711	0.18	90	0.30	0.15
17	NS	NS	NS		

Statistics

Assigned Value	0.68	0.10
Spike Value	0.694	0.035
Robust Average	0.68	0.10
Median	0.721	0.070
Mean	0.684	
N	10	
Max	0.82	
Min	0.49	
Robust SD	0.13	
Robust CV	19%	


Kernel Density
Density
Result
Results: S2 - Methomyl
Assigned Value = 0.68 ± 0.10 mg/kg
Results (mg/kg)
Laboratory
6 8 12 7 16 5 4 9 2 3 1 10 11 13 14 15 17 Md RA SV


z-Scores: S2 - Methomyl
Standard Deviation for Proficiency Assessment 0.10 mg/kg (Equivalent to 15% CV)
z-Score
-1.9 -1.7 -0.9 0.1 0.3 0.5 0.6 0.6 1.3 1.4
Laboratory
6 8 12 7 16 5 4 9 2 3

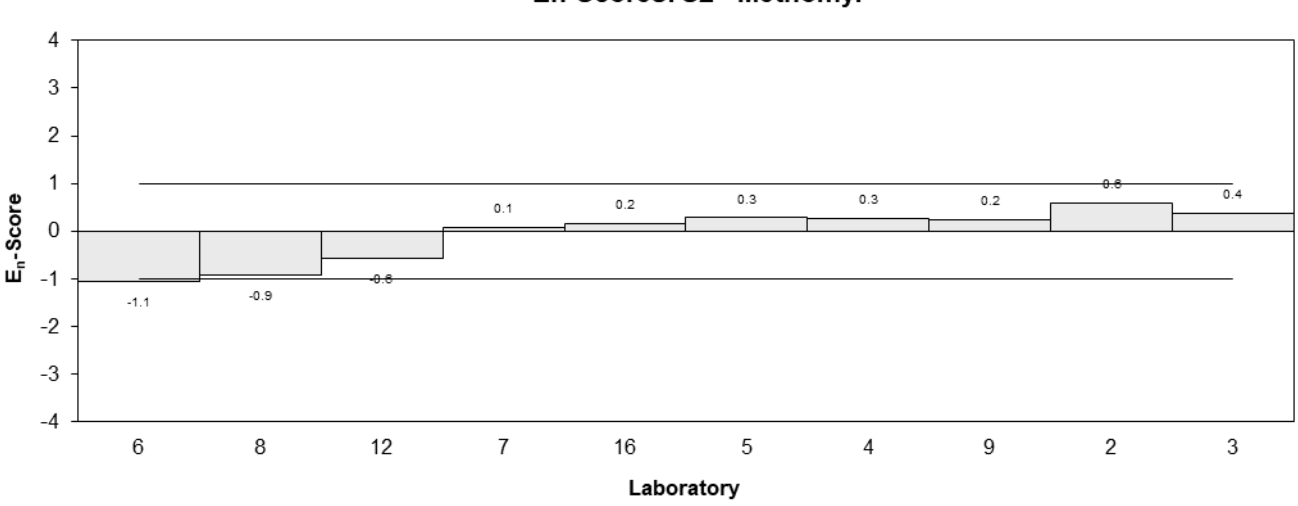

En-Scores: S2 - Methomyl
En-Score
-1.1 -0.9 -0.6 0.1 0.2 0.3 0.3 0.2 0.6 0.4
Laboratory
6 8 12 7 16 5 4 9 2 3

Figure 16

Table 21

Sample Details

Sample No.	S2
Matrix	Blueberry
Analyte	Phosmet
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	NT	NT	NT
2	NT	NT	NT
3	NT	NT	NT
4	3.8	0.5	99
5	2.5	0.5	NR
6	4.4	1.3	112
7	NT	NT	NT
8	1.5	0.45	68
9	3.7	1.5	79
10	2.8	1.4	112
11	NT	NT	NT
12	4.80	1.10	118
13	NT	NT	NT
14	NT	NT	NT
15	NS	NS	NS
16	NR	NR	NR
17	NS	NS	NS

Statistics

Assigned Value	Not Set	
Spike Value	3.98	0.20
Robust Average	3.4	1.2
Median	3.7	1.3
Mean	3.36	
N	7	
Max	4.8	
Min	1.5	
Robust SD	1.3	
Robust CV	39%	

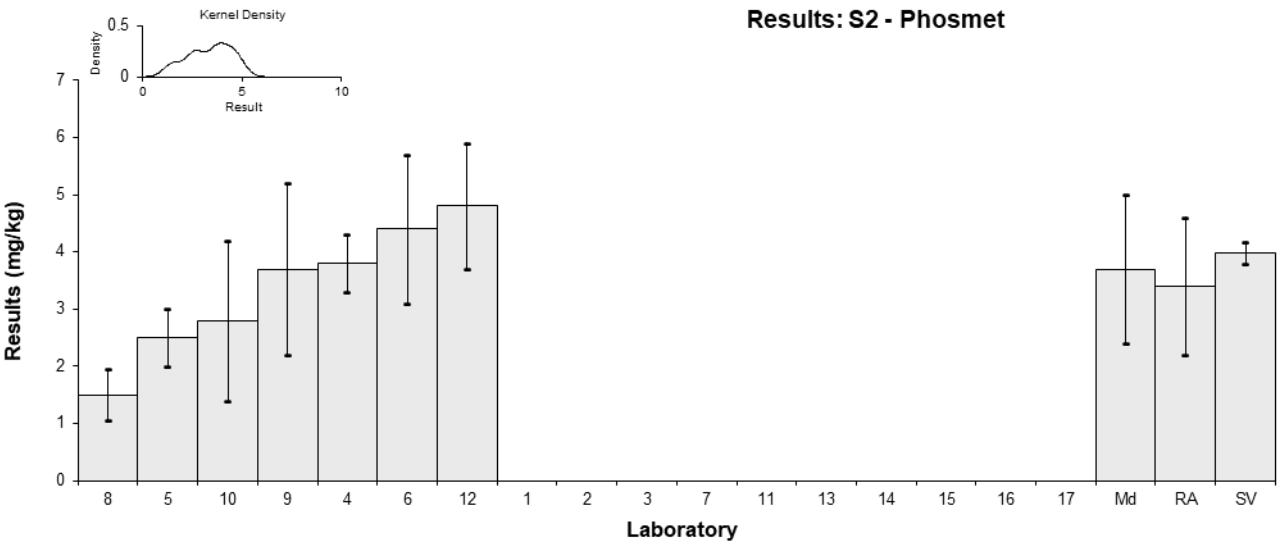

Results: S2 - Phosmet
Kernel Density
Density
0.5
0
0
5
10
Result
Results (mg/kg)
0
1
2
3
4
5
6
7
8
5
10
9
4
6
12
1
2
3
7
11
13
14
15
16
17
Md
RA
SV
Laboratory

Figure 17

Table 22

Sample Details

Sample No.	S2
Matrix	Blueberry
Analyte	Thiometon
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	NT	NT	NT
2	NT	NT	NT
3	NT	NT	NT
4	NT	NT	NT
5	0.42	0.084	NR
6	0.73	0.22	106
7	NT	NT	NT
8	NT	NT	NT
9	NT	NT	NT
10	NT	NT	NT
11	NT	NT	NT
12	0.41	0.08	90
13	NT	NT	NT
14	NT	NT	NT
15	NS	NS	NS
16	0.244	NR	88
17	NS	NS	NS

Statistics

Assigned Value	Not Set	
Spike Value	1.98	0.10
Robust Average	NA (N<6)	
Median	0.42	0.16
Mean	0.45	
N	4	
Max	0.73	
Min	0.244	
Robust SD	NA (N<6)	
Robust CV	NA (N<6)	

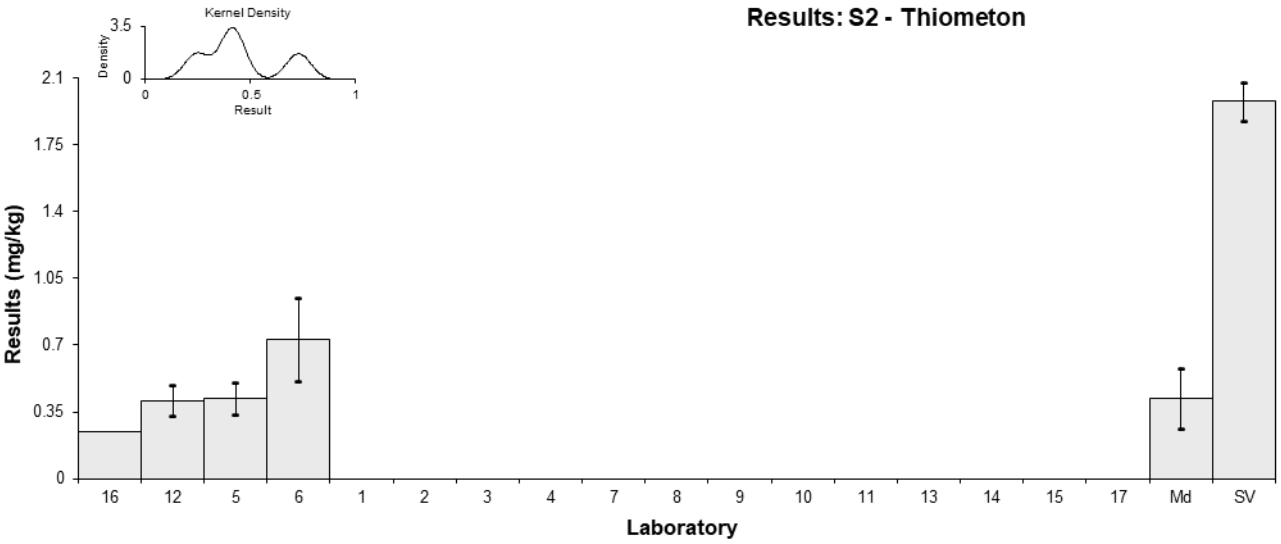

Results: S2 - Thiometon
Kernel Density
Density
3.5
0
0
0.5
1
Result
Results (mg/kg)
2.1
1.75
1.4
1.05
0.7
0.35
0
16
12
5
6
1
2
3
4
7
8
9
10
11
13
14
15
17
Md
SV
Laboratory

Figure 18

Table 23

Sample Details

Sample No.	S3
Matrix	Hemp Flour
Analyte	AMPA
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	NT	NT	NT
2	0.94	NR	NR
3	NS	NS	NS
4	NT	NT	NT
5	2.5	0.75	NR
6	NT	NT	NT
7	NT	NT	NT
8	NT	NT	NT
9	1.2	0.29	108
10	2.7	1.4	98
11	NS	NS	NS
12	2.80	0.70	120
13	NS	NS	NS
14	NS	NS	NS
15	2.8	0.84	98
16	NT	NT	NT
17	NS	NS	NS

Statistics

Assigned Value	Not Set	
Spike Value	3.01	0.15
Robust Average	2.16	0.99
Median	2.60	0.30
Mean	2.16	
N	6	
Max	2.8	
Min	0.94	
Robust SD	0.97	
Robust CV	45%	

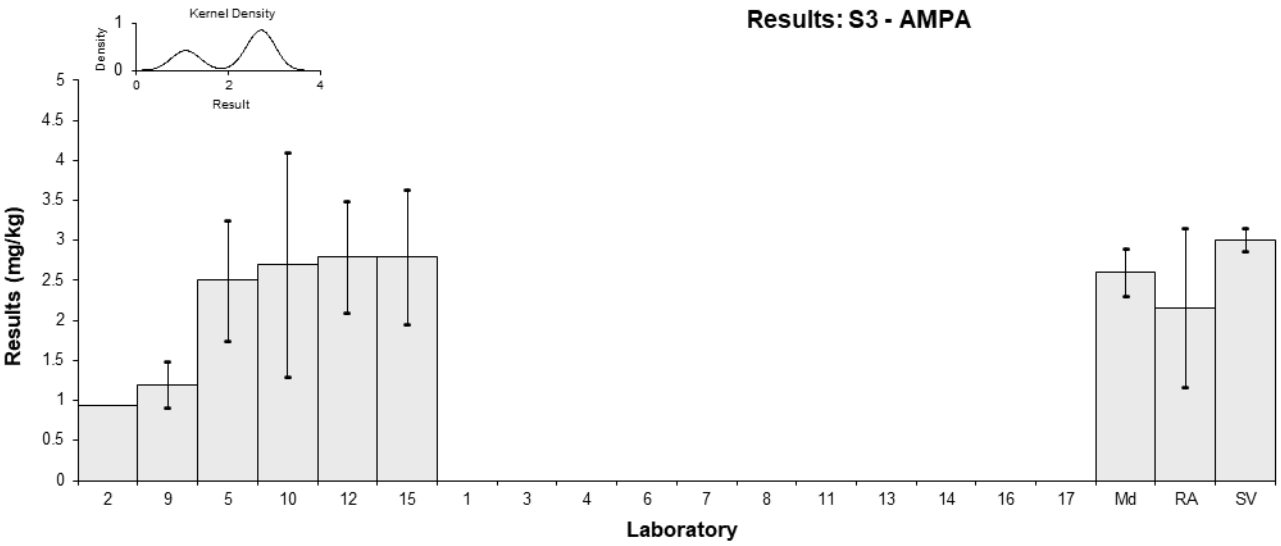

Results: S3 - AMPA
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
2
9
5
10
12
15
1
3
4
6
7
8
11
13
14
16
17
Md
RA
SV

Figure 19

Table 24

Sample Details

Sample No.	S3
Matrix	Hemp Flour
Analyte	Azoxystrobin
Unit	mg/kg

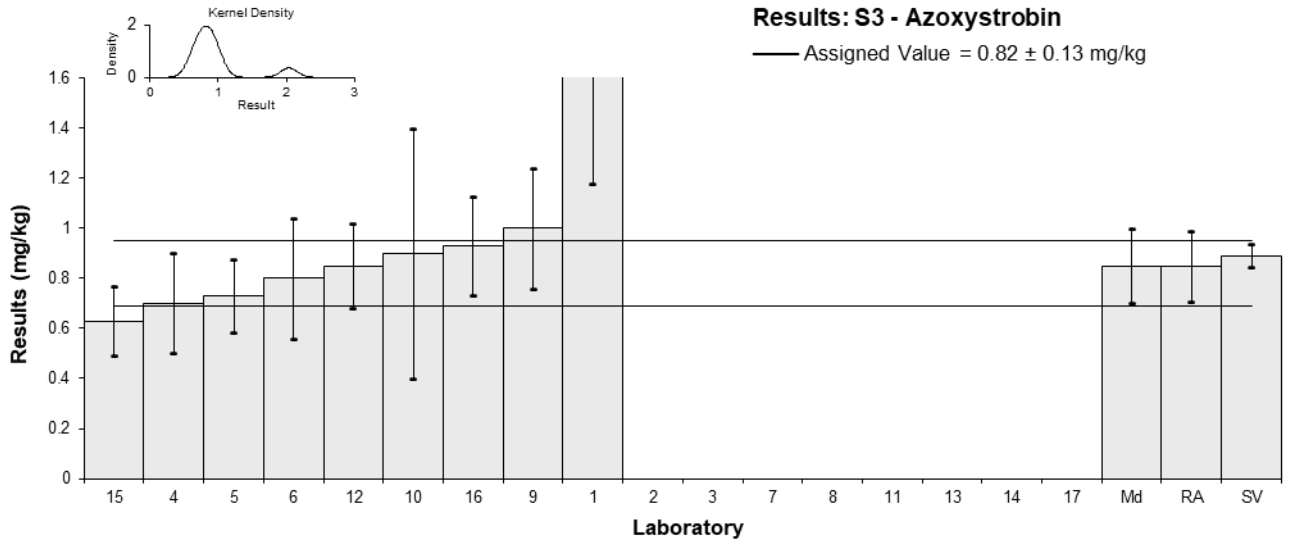
Participant Results

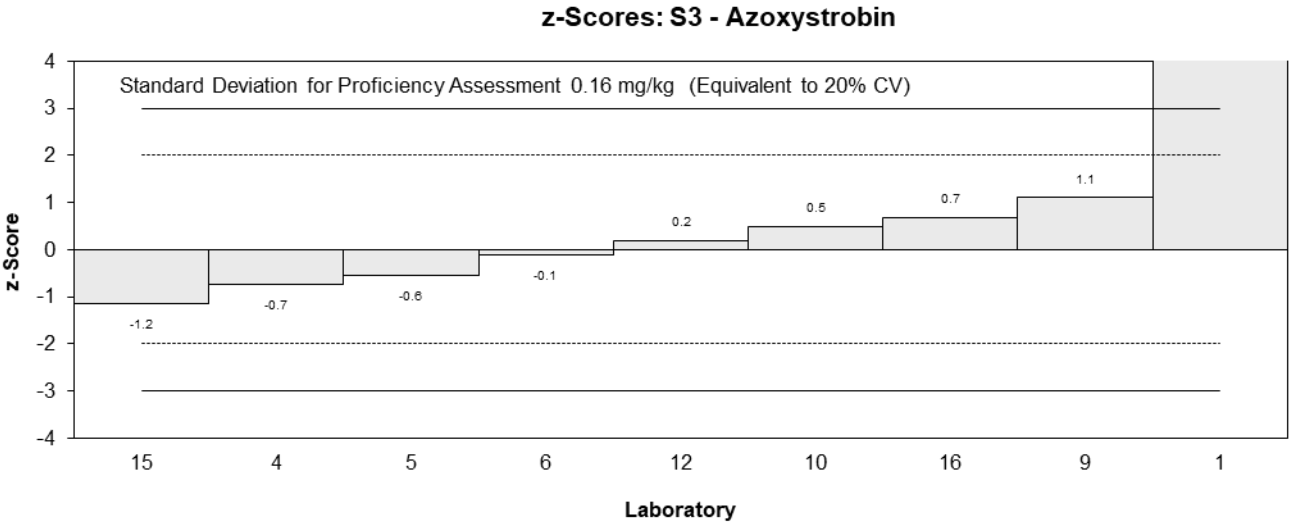
Lab. Code	Result	Uncertainty	Rec	z	E_n
1*	2.04	0.86	NR	7.44	1.40
2	NR	NR	NR		
3	NS	NS	NS		
4	0.7	0.2	91	-0.73	-0.50
5	0.73	0.146	NR	-0.55	-0.46
6	0.80	0.24	98	-0.12	-0.07
7	NT	NT	NT		
8	NT	NT	NT		
9	1.0	0.24	105	1.10	0.66
10	0.9	0.5	105	0.49	0.15
11	NS	NS	NS		
12	0.85	0.17	104	0.18	0.14
13	NS	NS	NS		
14	NS	NS	NS		
15	0.63	0.14	NR	-1.16	-0.99
16	0.931	0.198	91	0.68	0.47
17	NS	NS	NS		

* Outlier, see Section 4.2

Statistics

Assigned Value	0.82	0.13
Spike Value	0.892	0.045
Robust Average	0.85	0.14
Median	0.85	0.15
Mean	0.95	
N	9	
Max	2.04	
Min	0.63	
Robust SD	0.17	
Robust CV	20%	


Kernel Density
Density
Result
Results: S3 - Azoxystrobin
Assigned Value = 0.82 ± 0.13 mg/kg
Results (mg/kg)
Laboratory
15 4 5 6 12 10 16 9 1 2 3 7 8 11 13 14 17 Md RA SV


z-Scores: S3 - Azoxystrobin
Standard Deviation for Proficiency Assessment 0.16 mg/kg (Equivalent to 20% CV)
z-Score
-1.2
-0.7
-0.6
-0.1
0.2
0.5
0.7
1.1
Laboratory
15 4 5 6 12 10 16 9 1

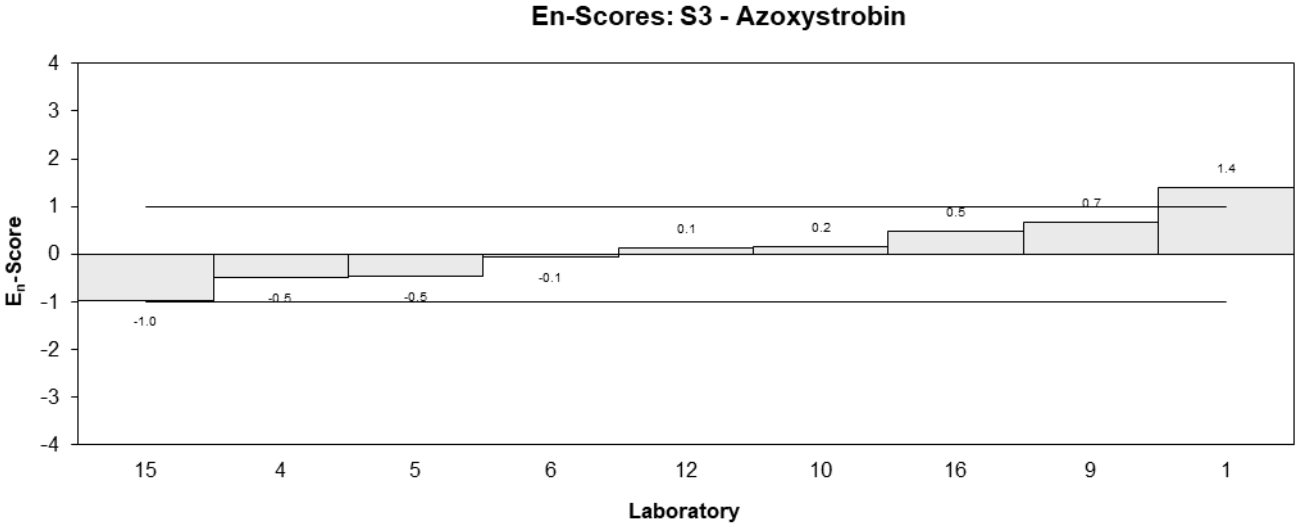

En-Scores: S3 - Azoxystrobin
En-Score
-1.0
-0.5
-0.5
-0.1
0.1
0.2
0.5
0.7
1.4
Laboratory
15 4 5 6 12 10 16 9 1

Figure 20

Table 25

Sample Details

Sample No.	S3
Matrix	Hemp Flour
Analyte	Chlordane
Unit	mg/kg

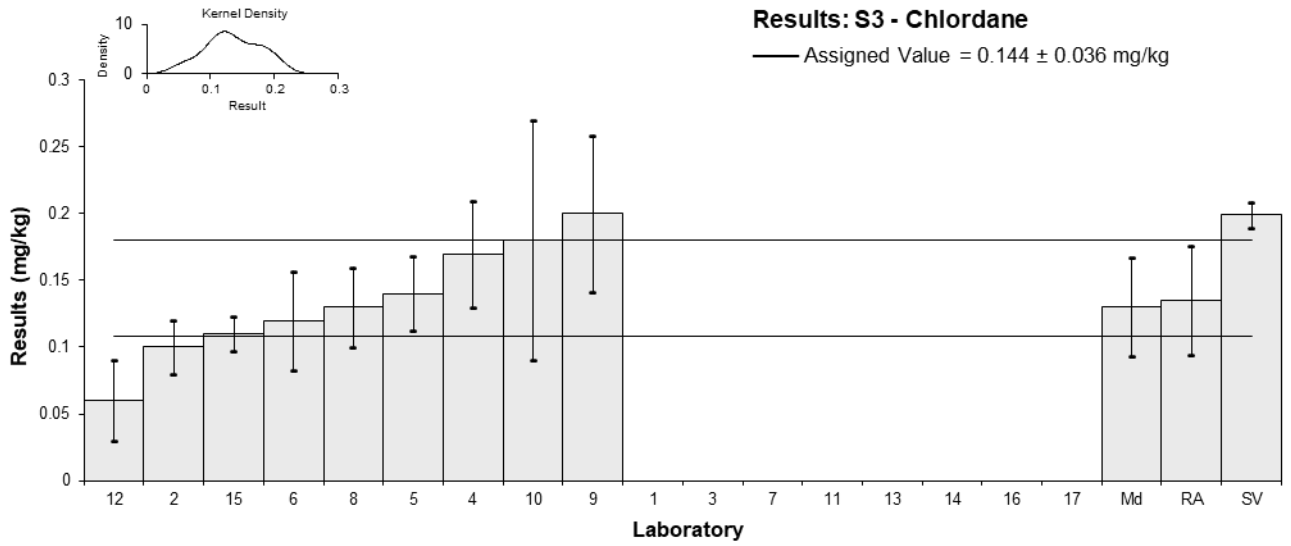
Participant Results

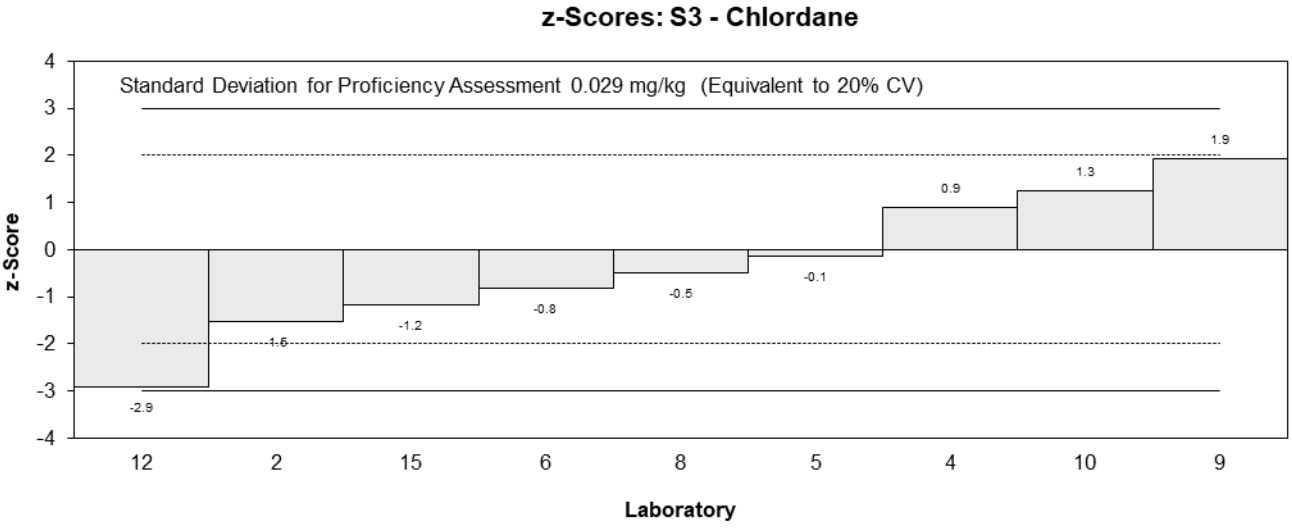
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	NT	NT	NT		
2	0.1	0.02	89	-1.53	-1.07
3	NS	NS	NS		
4	0.17	0.04	93	0.90	0.48
5	0.14	0.028	NR	-0.14	-0.09
6	0.12	0.037	101	-0.83	-0.46
7	NT	NT	NT		
8	0.13	0.03	83	-0.49	-0.30
9	0.20	0.059	46	1.94	0.81
10	0.18	0.09	81	1.25	0.37
11	NS	NS	NS		
12*	0.060	0.030	66	-2.92	-1.79
13	NS	NS	NS		
14	NS	NS	NS		
15	0.11	0.013	NR	-1.18	-0.89
16	NR	NR	NR		
17	NS	NS	NS		

* Outlier, see Section 4.2

Statistics

Assigned Value	0.144	0.036
Spike Value	0.199	0.010
Robust Average	0.135	0.041
Median	0.130	0.037
Mean	0.134	
N	9	
Max	0.2	
Min	0.06	
Robust SD	0.049	
Robust CV	37%	


Kernel Density
Density
Result
Results: S3 - Chlordane
Assigned Value = 0.144 ± 0.036 mg/kg
Results (mg/kg)
Laboratory
12 2 15 6 8 5 4 10 9 1 3 7 11 13 14 16 17 Md RA SV


z-Scores: S3 - Chlordane
Standard Deviation for Proficiency Assessment 0.029 mg/kg (Equivalent to 20% CV)
z-Score
Laboratory
12 2 15 6 8 5 4 10 9
-2.9
-1.5
-1.2
-0.8
-0.5
-0.1
0.9
1.3
1.9

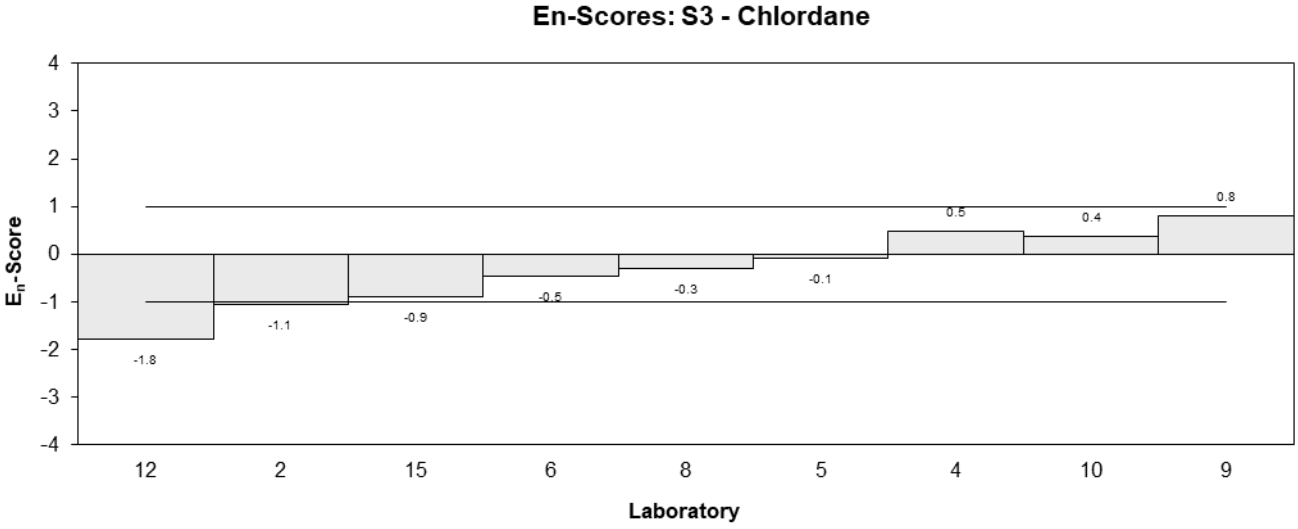

En-Scores: S3 - Chlordane
En-Score
Laboratory
12 2 15 6 8 5 4 10 9
-1.8
-1.1
-0.9
-0.5
-0.3
-0.1
0.5
0.4
0.8

Figure 21

Table 26

Sample Details

Sample No.	S3
Matrix	Hemp Flour
Analyte	Cypermethrin
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	1.53	0.43	104
2	12.18	1.9	87
3	NS	NS	NS
4	2.1	0.3	94
5	1.28	0.256	NR
6	2.3	0.93	140
7	NT	NT	NT
8	<3	NR	NR
9	1.2	0.37	78
10	2.5	1.3	126
11	NS	NS	NS
12	1.27	0.30	70
13	NS	NS	NS
14	NS	NS	NS
15	1.4	0.53	NR
16	NR	NR	NR
17	NS	NS	NS

Statistics

Assigned Value	Not Set	
Spike Value	2.01	0.10
Robust Average	1.83	0.60
Median	1.53	0.41
Mean	2.9	
N	9	
Max	12.18	
Min	1.2	
Robust SD	0.72	
Robust CV	39%	

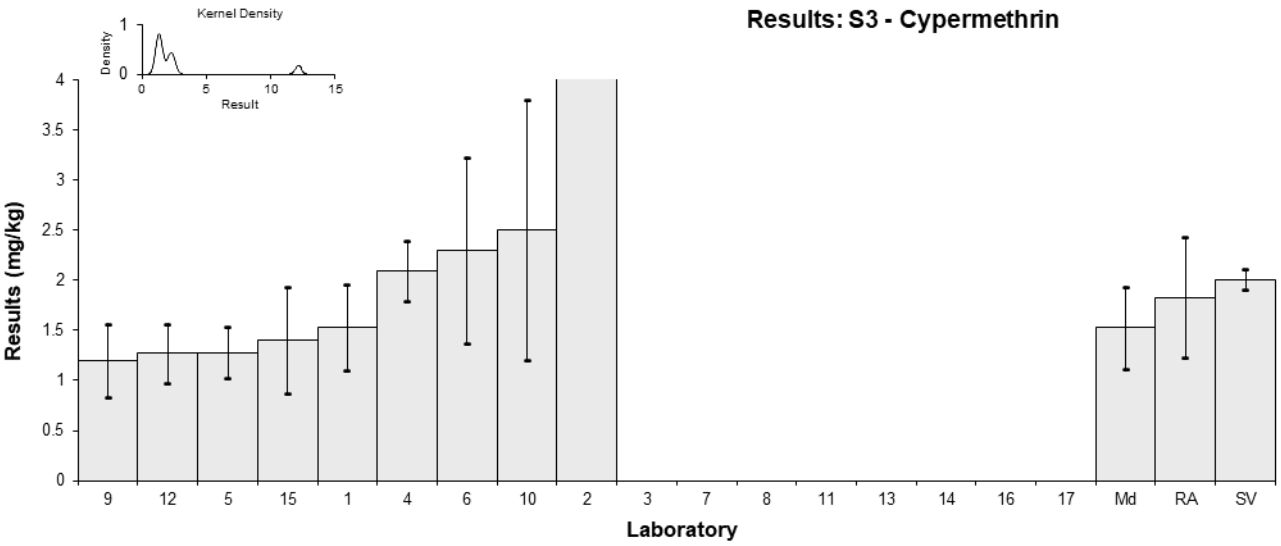

Results: S3 - Cypermethrin
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
9
12
5
15
1
4
6
10
2
3
7
8
11
13
14
16
17
Md
RA
SV

Figure 22

Table 27

Sample Details

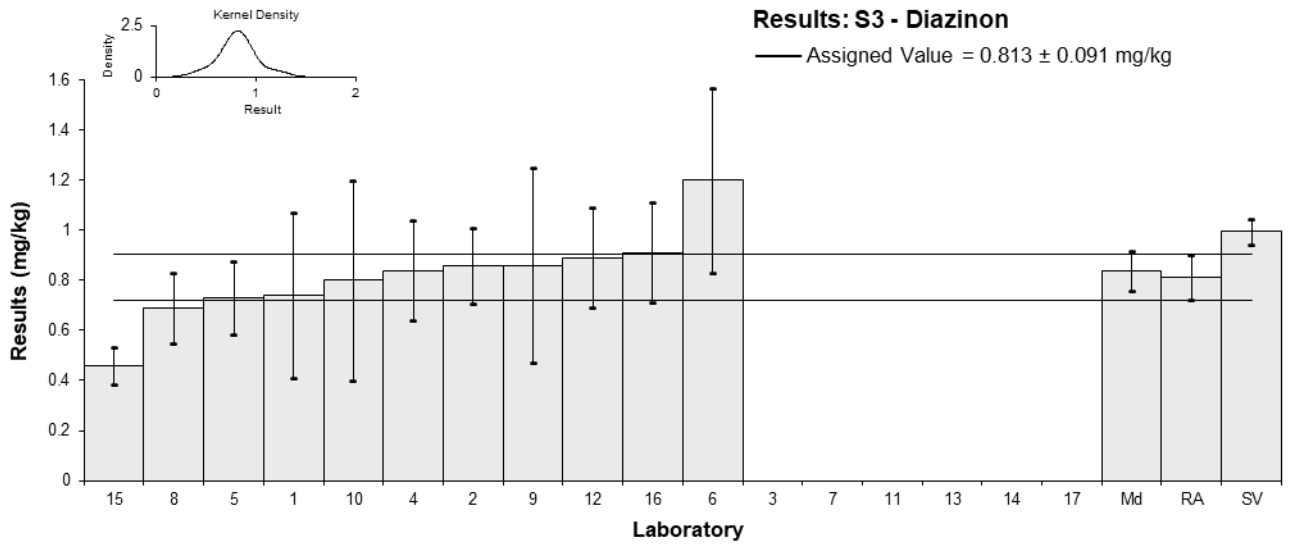
Sample No.	S3
Matrix	Hemp Flour
Analyte	Diazinon
Unit	mg/kg

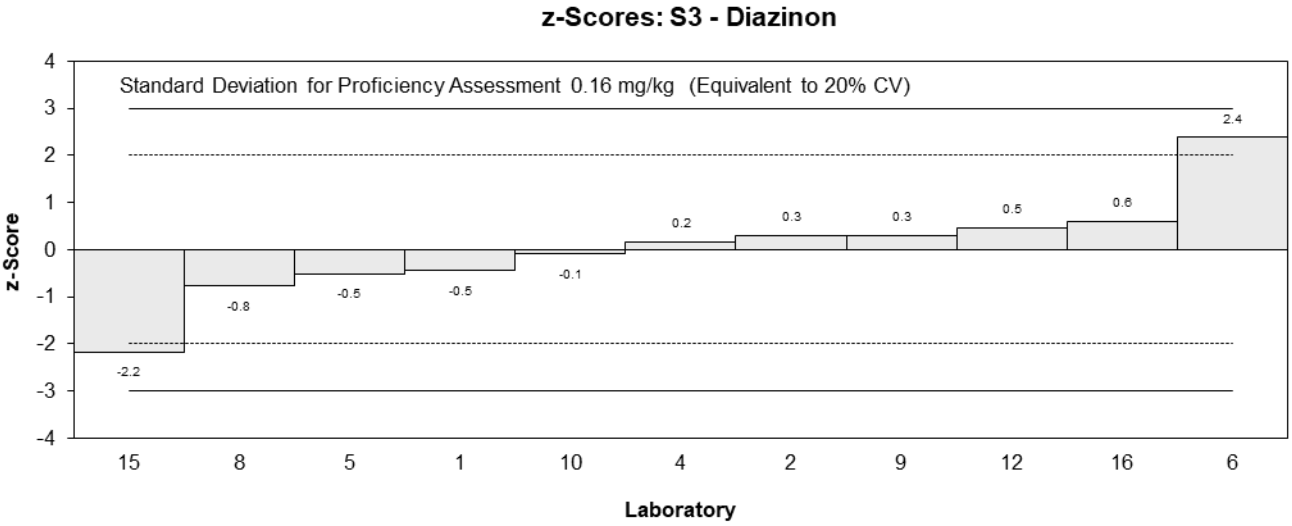
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.74	0.33	103	-0.45	-0.21
2	0.86	0.15	89	0.29	0.27
3	NS	NS	NS		
4	0.84	0.2	97	0.17	0.12
5	0.73	0.146	NR	-0.51	-0.48
6	1.2	0.37	93	2.38	1.02
7	NT	NT	NT		
8	0.69	0.14	83	-0.76	-0.74
9	0.86	0.39	95	0.29	0.12
10	0.8	0.4	99	-0.08	-0.03
11	NS	NS	NS		
12	0.89	0.20	92	0.47	0.35
13	NS	NS	NS		
14	NS	NS	NS		
15	0.46	0.074	NR	-2.17	-3.01
16	0.911	0.2	93	0.60	0.45
17	NS	NS	NS		

Statistics

Assigned Value	0.813	0.091
Spike Value	0.995	0.050
Robust Average	0.813	0.091
Median	0.840	0.079
Mean	0.82	
N	11	
Max	1.2	
Min	0.46	
Robust SD	0.12	
Robust CV	15%	


Kernel Density
Density
Result
Results: S3 - Diazinon
Assigned Value = 0.813 ± 0.091 mg/kg
Results (mg/kg)
Laboratory
15 8 5 1 10 4 2 9 12 16 6 3 7 11 13 14 17 Md RA SV


z-Scores: S3 - Diazinon
Standard Deviation for Proficiency Assessment 0.16 mg/kg (Equivalent to 20% CV)
z-Score
Laboratory
15 8 5 1 10 4 2 9 12 16 6
-2.2 -0.8 -0.5 -0.5 -0.1 0.2 0.3 0.3 0.5 0.6 2.4

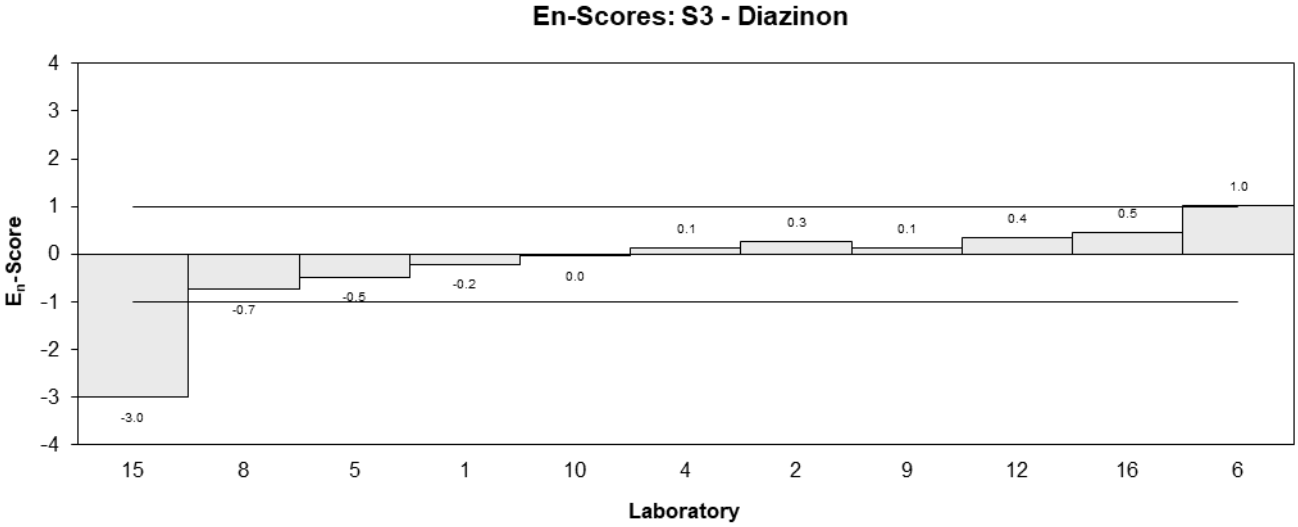

En-Scores: S3 - Diazinon
En-Score
Laboratory
15 8 5 1 10 4 2 9 12 16 6
-3.0 -0.7 -0.5 -0.2 0.0 0.1 0.3 0.1 0.4 0.5 1.0

Figure 23

Table 28

Sample Details

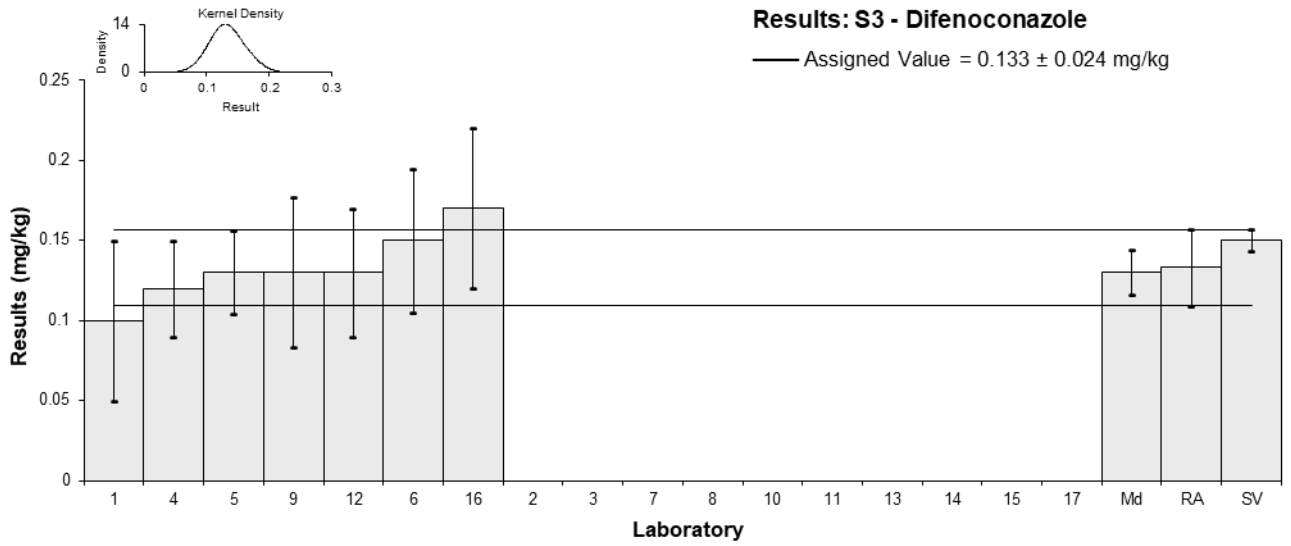
Sample No.	S3
Matrix	Hemp Flour
Analyte	Difenoconazole
Unit	mg/kg

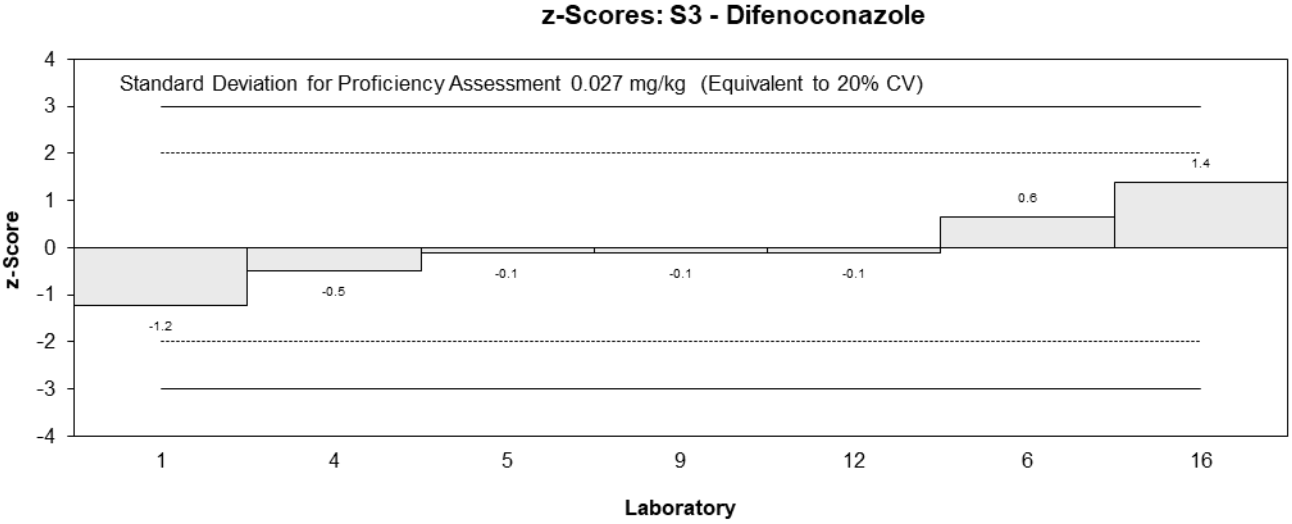
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.1	0.05	111	-1.24	-0.60
2	NR	NR	NR		
3	NS	NS	NS		
4	0.12	0.03	101	-0.49	-0.34
5	0.13	0.026	NR	-0.11	-0.08
6	0.15	0.045	92	0.64	0.33
7	NT	NT	NT		
8	NT	NT	NT		
9	0.13	0.047	128	-0.11	-0.06
10	NT	NT	NT		
11	NS	NS	NS		
12	0.13	0.040	92	-0.11	-0.06
13	NS	NS	NS		
14	NS	NS	NS		
15	NT	NT	NT		
16	0.17	0.05	98	1.39	0.67
17	NS	NS	NS		

Statistics

Assigned Value	0.133	0.024
Spike Value	0.150	0.007
Robust Average	0.133	0.024
Median	0.130	0.014
Mean	0.133	
N	7	
Max	0.17	
Min	0.1	
Robust SD	0.025	
Robust CV	19%	


Kernel Density
Density
Result
Results: S3 - Difenoconazole
Assigned Value = 0.133 ± 0.024 mg/kg
Results (mg/kg)
Laboratory
1 4 5 9 12 6 16 2 3 7 8 10 11 13 14 15 17 Md RA SV


z-Scores: S3 - Difenoconazole
Standard Deviation for Proficiency Assessment 0.027 mg/kg (Equivalent to 20% CV)
z-Score
-1.2
-0.5
-0.1
-0.1
-0.1
0.6
1.4
Laboratory
1 4 5 9 12 6 16

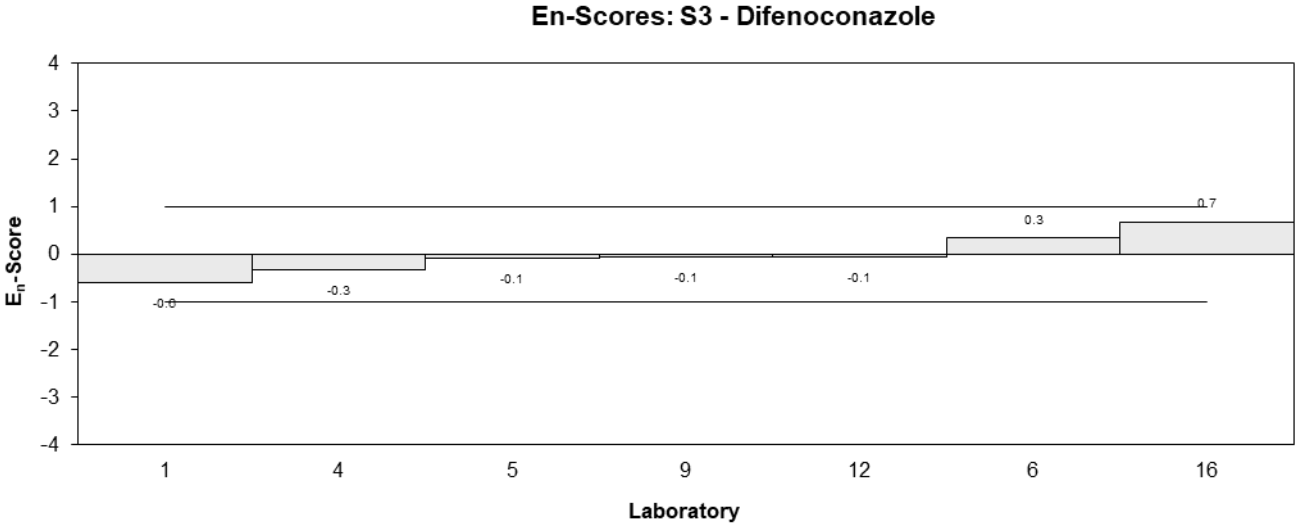

En-Scores: S3 - Difenoconazole
En-Score
-0.6
-0.3
-0.1
-0.1
-0.1
0.3
0.7
Laboratory
1 4 5 9 12 6 16

Figure 24

Table 29

Sample Details

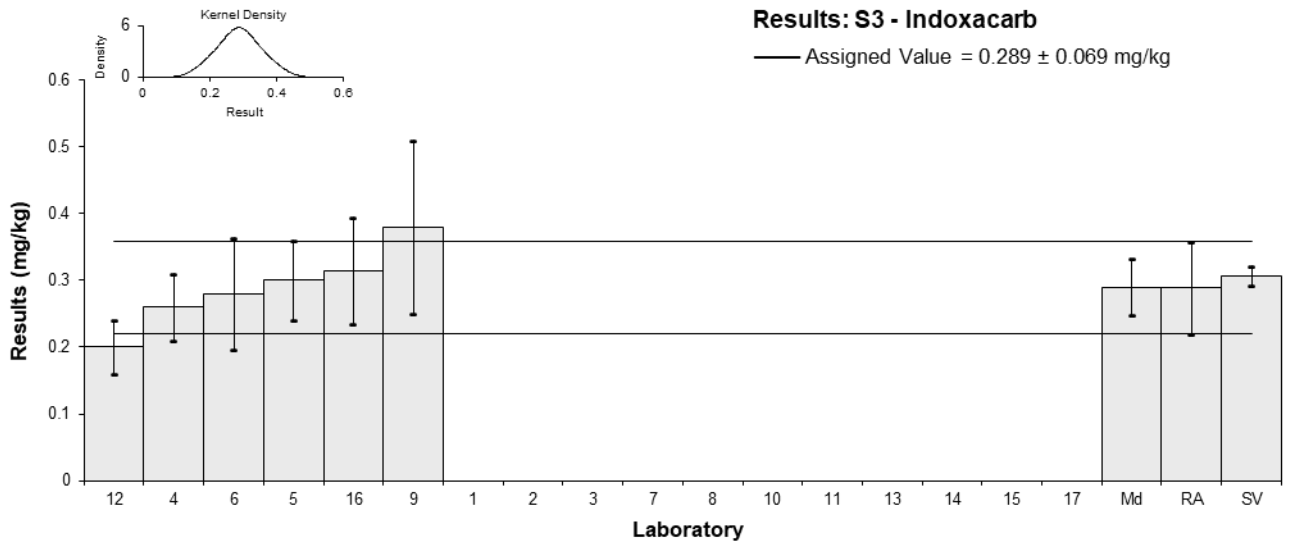
Sample No.	S3
Matrix	Hemp Flour
Analyte	Indoxacarb
Unit	mg/kg

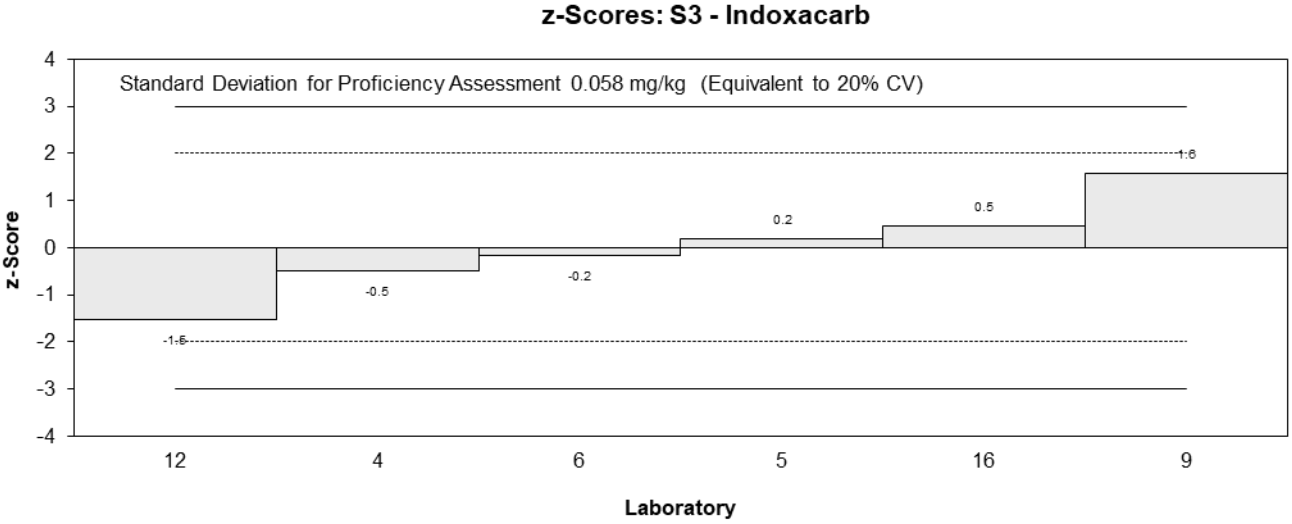
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	NR	NR	NR		
2	NR	NR	NR		
3	NS	NS	NS		
4	0.26	0.05	93	-0.50	-0.34
5	0.3	0.06	NR	0.19	0.12
6	0.28	0.084	102	-0.16	-0.08
7	NT	NT	NT		
8	NT	NT	NT		
9	0.38	0.13	105	1.57	0.62
10	NT	NT	NT		
11	NS	NS	NS		
12	0.20	0.040	76	-1.54	-1.12
13	NS	NS	NS		
14	NS	NS	NS		
15	NT	NT	NT		
16	0.315	0.08	98	0.45	0.25
17	NS	NS	NS		

Statistics

Assigned Value	0.289	0.069
Spike Value	0.307	0.015
Robust Average	0.289	0.069
Median	0.290	0.042
Mean	0.289	
N	6	
Max	0.38	
Min	0.2	
Robust SD	0.068	
Robust CV	23%	


Kernel Density
Density
Result
Results: S3 - Indoxacarb
Assigned Value = 0.289 ± 0.069 mg/kg
Results (mg/kg)
Laboratory
12
4
6
5
16
9
1
2
3
7
8
10
11
13
14
15
17
Md
RA
SV


z-Scores: S3 - Indoxacarb
Standard Deviation for Proficiency Assessment 0.058 mg/kg (Equivalent to 20% CV)
z-Score
Laboratory
12
4
6
5
16
9
-1.5
-0.5
-0.2
0.2
0.5
1.6

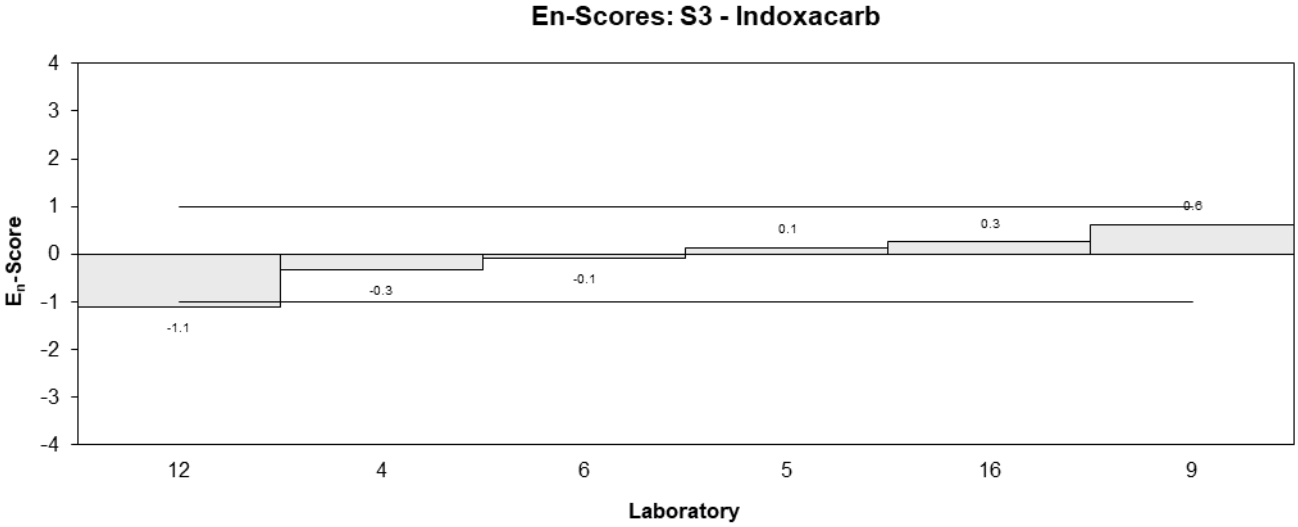

En-Scores: S3 - Indoxacarb
En-Score
Laboratory
12
4
6
5
16
9
-1.1
-0.3
-0.1
0.1
0.3
0.6

Figure 25

Table 30

Sample Details

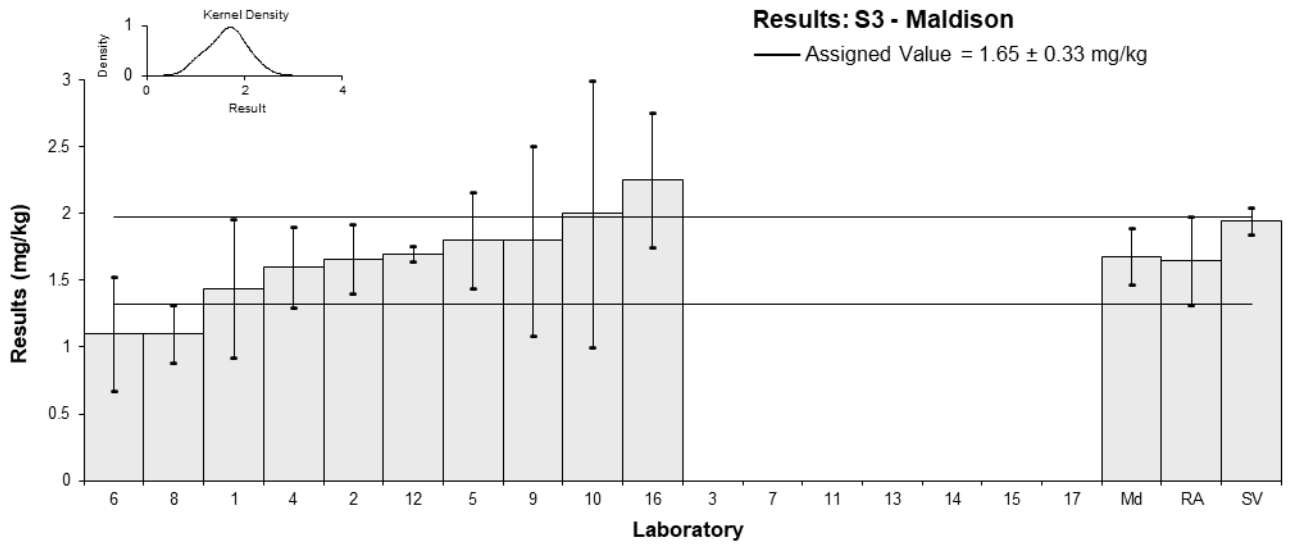
Sample No.	S3
Matrix	Hemp Flour
Analyte	Maldison
Unit	mg/kg

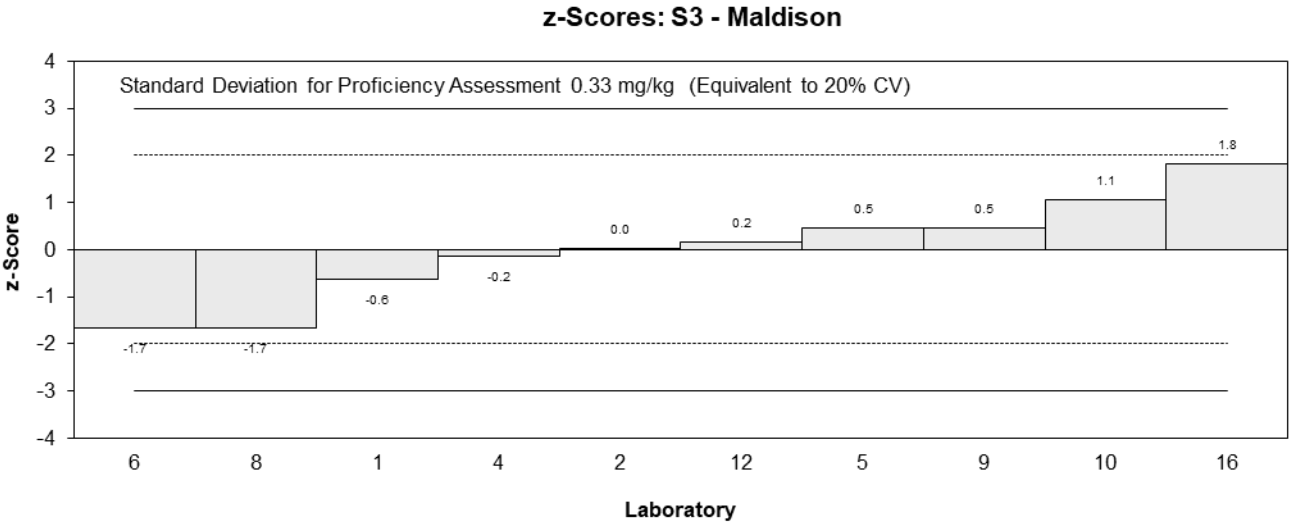
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	1.44	0.52	96	-0.64	-0.34
2	1.66	0.26	90	0.03	0.02
3	NS	NS	NS		
4	1.6	0.3	94	-0.15	-0.11
5	1.8	0.36	NR	0.45	0.31
6	1.1	0.43	134	-1.67	-1.01
7	NT	NT	NT		
8	1.1	0.22	88	-1.67	-1.39
9	1.8	0.71	102	0.45	0.19
10	2.0	1	119	1.06	0.33
11	NS	NS	NS		
12	1.70	0.060	76	0.15	0.15
13	NS	NS	NS		
14	NS	NS	NS		
15	<1	NR	NR		
16	2.254	0.5	89	1.83	1.01
17	NS	NS	NS		

Statistics

Assigned Value	1.65	0.33
Spike Value	1.95	0.10
Robust Average	1.65	0.33
Median	1.68	0.21
Mean	1.65	
N	10	
Max	2.254	
Min	1.1	
Robust SD	0.41	
Robust CV	25%	


Kernel Density
Density
Result
Results: S3 - Maldison
Assigned Value = 1.65 ± 0.33 mg/kg
Results (mg/kg)
Laboratory
6 8 1 4 2 12 5 9 10 16 3 7 11 13 14 15 17 Md RA SV


z-Scores: S3 - Maldison
Standard Deviation for Proficiency Assessment 0.33 mg/kg (Equivalent to 20% CV)
z-Score
-1.7 -1.7 -0.6 -0.2 0.0 0.2 0.5 0.5 1.1 1.8
Laboratory
6 8 1 4 2 12 5 9 10 16

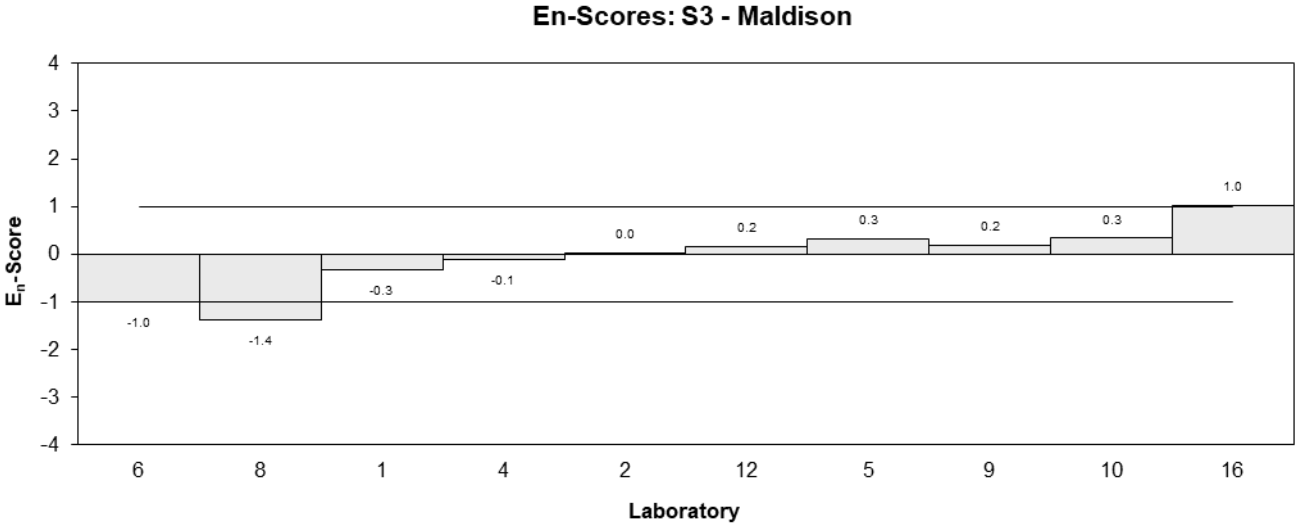

En-Scores: S3 - Maldison
En-Score
-1.0 -1.4 -0.3 -0.1 0.0 0.2 0.3 0.2 0.3 1.0
Laboratory
6 8 1 4 2 12 5 9 10 16

Figure 26

Table 31

Sample Details

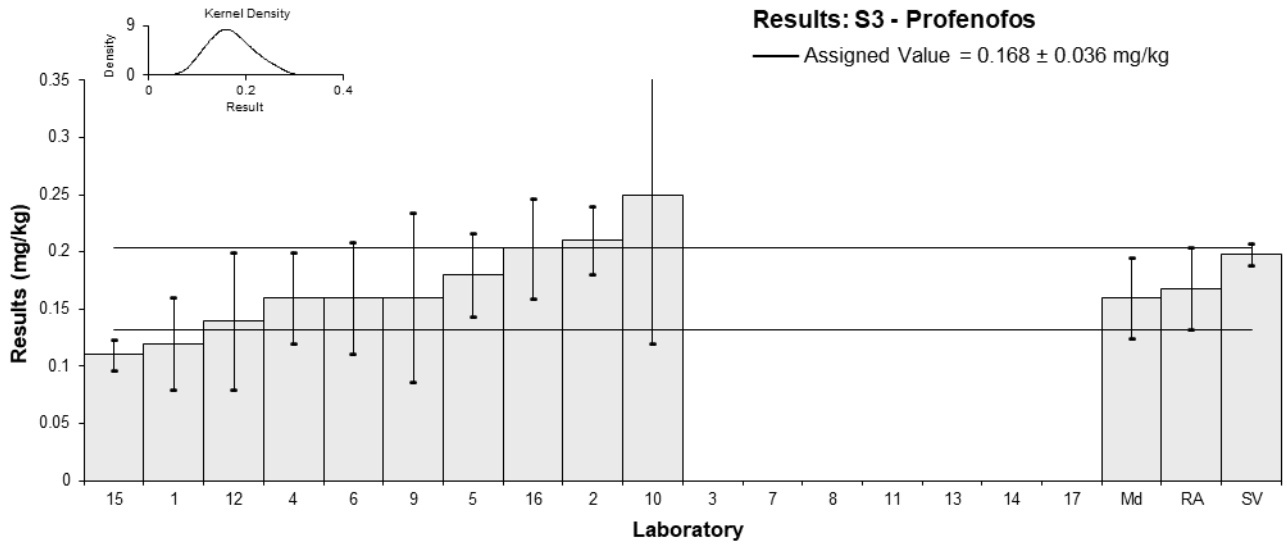
Sample No.	S3
Matrix	Hemp Flour
Analyte	Profenofos
Unit	mg/kg

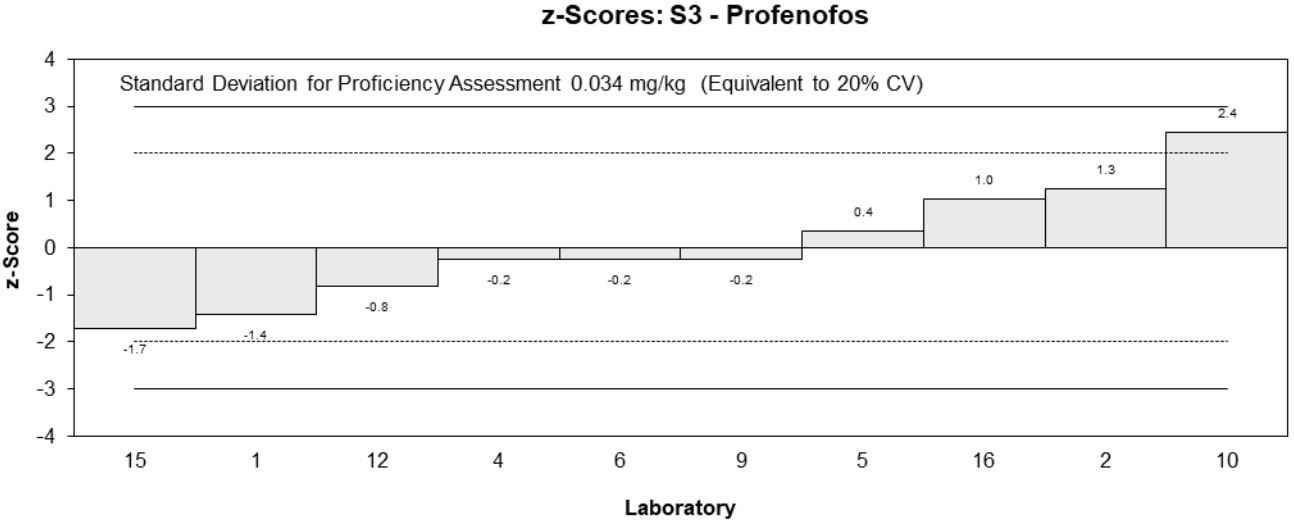
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.12	0.04	101	-1.43	-0.89
2	0.21	0.03	82	1.25	0.90
3	NS	NS	NS		
4	0.16	0.04	94	-0.24	-0.15
5	0.18	0.036	NR	0.36	0.24
6	0.16	0.049	98	-0.24	-0.13
7	NT	NT	NT		
8	<0.1	NR	NR		
9	0.16	0.074	109	-0.24	-0.10
10	0.25	0.13	128	2.44	0.61
11	NS	NS	NS		
12	0.14	0.060	78	-0.83	-0.40
13	NS	NS	NS		
14	NS	NS	NS		
15	0.11	0.013	NR	-1.73	-1.52
16	0.203	0.044	114	1.04	0.62
17	NS	NS	NS		

Statistics

Assigned Value	0.168	0.036
Spike Value	0.198	0.010
Robust Average	0.168	0.036
Median	0.160	0.035
Mean	0.169	
N	10	
Max	0.25	
Min	0.11	
Robust SD	0.045	
Robust CV	27%	


Kernel Density
Density
Result
Results: S3 - Profenofos
Assigned Value = 0.168 ± 0.036 mg/kg
Results (mg/kg)
Laboratory
15 1 12 4 6 9 5 16 2 10 3 7 8 11 13 14 17 Md RA SV


z-Scores: S3 - Profenofos
Standard Deviation for Proficiency Assessment 0.034 mg/kg (Equivalent to 20% CV)
z-Score
Laboratory
15 1 12 4 6 9 5 16 2 10
-1.7 -1.4 -0.8 -0.2 -0.2 -0.2 0.4 1.0 1.3 2.4

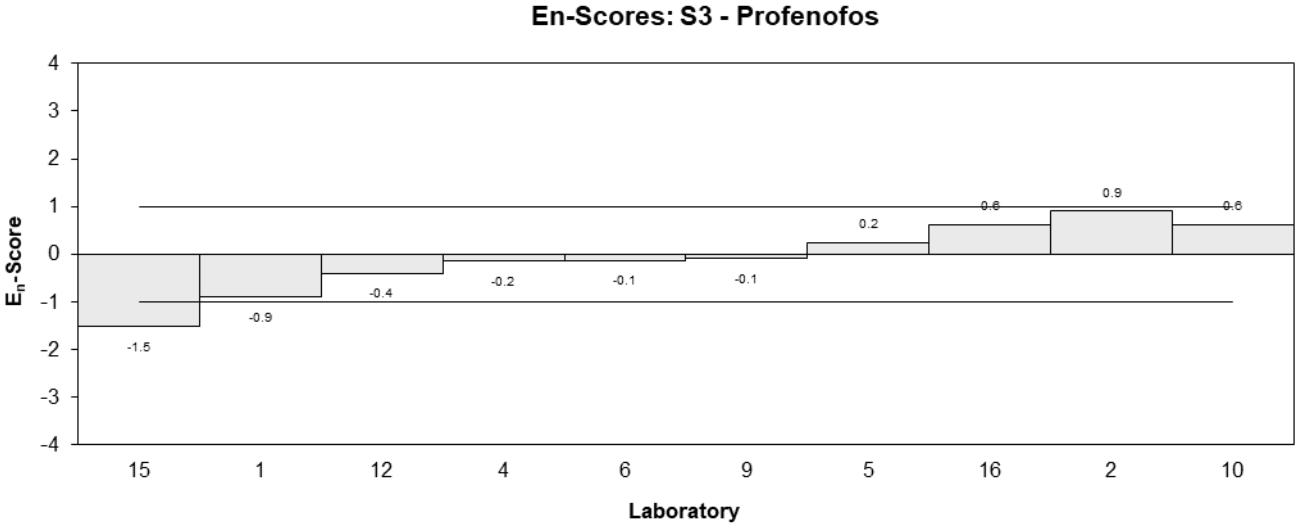

En-Scores: S3 - Profenofos
En-Score
Laboratory
15 1 12 4 6 9 5 16 2 10
-1.5 -0.9 -0.4 -0.2 -0.1 -0.1 0.2 0.6 0.9 0.6

Figure 27

Table 32

Sample Details

Sample No.	S4
Matrix	Garlic
Analyte	Maleic hydrazide
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	NS	NS	NS
2	NT	NT	NT
3	NS	NS	NS
4	NS	NS	NS
5	0.72	0.216	NR
6	4.2	1.3	90
7	NS	NS	NS
8	NS	NS	NS
9	NS	NS	NS
10	NS	NS	NS
11	NS	NS	NS
12	2.80	0.98	124
13	NS	NS	NS
14	NS	NS	NS
15	NS	NS	NS
16	NS	NS	NS
17	1.1	0.6	101

Statistics

Assigned Value	Not Set	
Spike Value	12.9	0.6
Robust Average	NA (N<6)	
Median	2.0	1.9
Mean	2.2	
N	4	
Max	4.2	
Min	0.72	
Robust SD	NA (N<6)	
Robust CV	NA (N<6)	

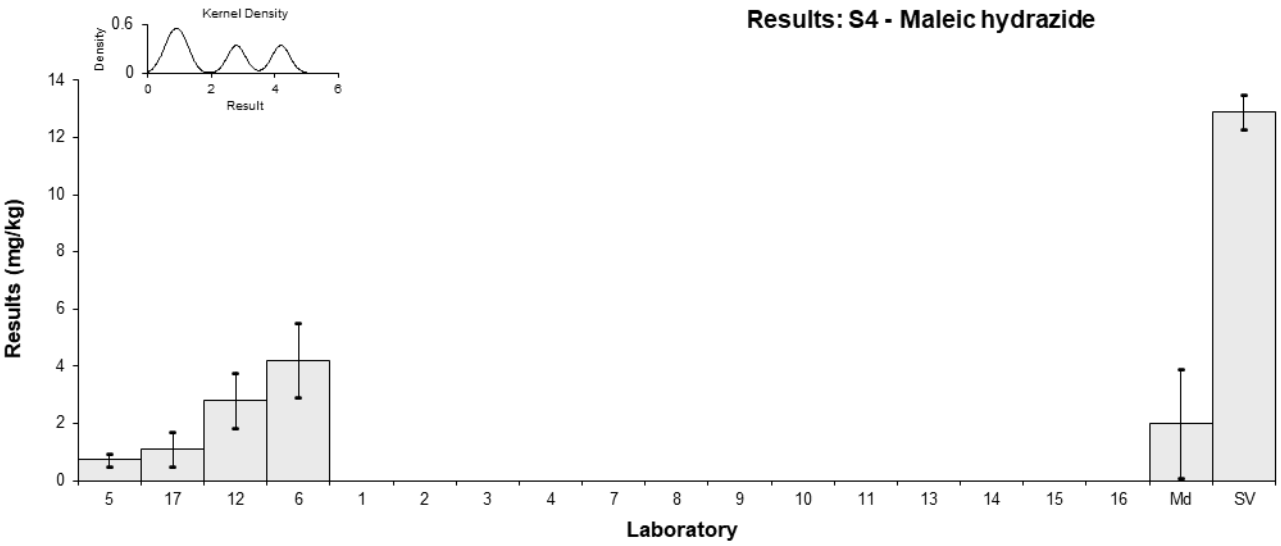

Results: S4 - Maleic hydrazide
Kernel Density
Density
0.6
0
0
2
4
6
Result
Results (mg/kg)
14
12
10
8
6
4
2
0
5
17
12
6
1
2
3
4
7
8
9
10
11
13
14
15
16
Md
SV
Laboratory

Figure 28

6 DISCUSSION OF RESULTS

6.1 Assigned Value

Assigned values for all scored analytes were the robust averages of participants' results. Results less than 50% or greater than 150% of the robust average were excluded from the calculation of the assigned values.[3,4] The robust averages and associated expanded uncertainties were calculated using the procedure described in ISO 13528.[7] The calculation of the expanded uncertainty for robust averages is presented in Appendix 3, using Sample S3 profenofos as an example.

No assigned values were set for Sample S1 abamectin, Sample S2 bifenthrin, phosmet and thiometon, and Sample S3 AMPA and cypermethrin, as the reported results were too few or too variable.

No assigned value was set for Sample S4 either. This sample was a pilot sample designed to support laboratories in developing their methods for this test. Laboratories can still compare their results against those of other participants, as well as the spiked values, as presented in Section 5.

A comparison of the assigned values and the spiked values is presented in Table 33. Assigned values for scored analytes were between 63% and 108% of the spiked values, which is similar to ratios observed in previous NMIA PT studies.

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.

Table 33 Comparison of Assigned Values and Spiked Values

Sample	Analyte	Assigned Value (mg/kg)	Spiked Value (mg/kg)	Assigned Value / Spiked Value (%)
S1	Abamectin	0.0235*	0.0305	77
S1	Acephate	0.0470	0.0504	93
S1	Buprofezin	0.76	0.856	89
S1	Endosulfan	0.0366	0.0398	92
S1	Fenvalerate	0.0536	0.0607	88
S1	Imidacloprid	0.0209	0.0200	105
S1	Indoxacarb	0.256	0.300	85
S1	Methomyl	0.442	0.700	63
S2	Chlorpyrifos	0.0292	0.0302	97
S2	Cyprodinil	0.0568	0.0615	92
S2	Dimethoate	0.513	0.497	103
S2	Imidacloprid	0.0213	0.0198	108
S2	Maldison	1.69	1.97	86
S2	Methomyl	0.68	0.694	98
S2	Phosmet	3.4*	3.98	85
S2	Thiometon	0.42*	1.98	21
S3	AMPA	2.16*	3.01	72
S3	Azoxystrobin	0.82	0.892	92

Sample	Analyte	Assigned Value (mg/kg)	Spiked Value (mg/kg)	Assigned Value / Spiked Value (%)
S3	Chlordane	0.144	0.199	72
S3	Cypermethrin	1.83*	2.01	91
S3	Diazinon	0.813	0.995	82
S3	Difenoconazole	0.133	0.150	89
S3	Indoxacarb	0.289	0.307	94
S3	Maldison	1.65	1.95	85
S3	Profenofos	0.168	0.198	85
S4	Maleic hydrazide	2.0*	12.9	16

*Robust average or median value as applicable (assigned value not set).

6.2 Measurement Uncertainty Reported by Participants

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

Of 269 numeric results reported for the analytes of interest in this study, 265 (99%) were reported with an associated expanded MU. Participants used a wide variety of procedures to evaluate their uncertainty (Tables 3 and 4).

Participants were requested to report absolute expanded uncertainties in units of mg/kg. Laboratory 7 reported some uncertainties as relative uncertainties (i.e. uncertainties were reported as '*x*%'); for consistency, these uncertainties have been converted to absolute uncertainties. Caution should be exercised when the result and uncertainties are reported in different units as this can be misleading.

The magnitude of the reported uncertainties for spiked analytes in this study was within the range 3.5% to 200%. In general, an expanded uncertainty of less than 15% relative may be unrealistically small for measurements of a pesticide residue using routine methods, while over 50% may be too large to be fit for purpose.

Laboratory **7** should review the procedure they used for evaluating and reporting uncertainties, as some of the uncertainties they reported were larger than the result itself.

Laboratories 12 and 16 should also review the procedure they use to evaluate and report uncertainties, as some of the uncertainties they reported were unrealistically small.

Uncertainties associated with results returning an acceptable *z*-score but a not acceptable 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 0.0353 ± 0.0136 mg/kg, it is recommended to report this as 0.035 ± 0.014 mg/kg.[10]

6.3 z-Scores

The *z*-score compares the participant's deviation from the assigned value based on the standard deviation for proficiency assessment (SDPA). The SDPA defines acceptable

performance in a PT study. SDPAs equivalent to 15% (Samples S1 and S2) and 20% (Sample S3) performance coefficient of variation (PCV) were used to calculate *z*-scores in this study. Unlike the standard deviation based on between-laboratory CV, setting the SDPA as a realistic value enables *z*-scores to be used as fixed reference value points for assessment of individual laboratory performance, independent of the group's performance.

The CVs predicted by the Thompson-Horwitz equation,[8] between-laboratory CVs in this study, and the SDPAs (as PCV), are presented for comparison in Table 34.

Table 34 Comparison of Between-Laboratory CV, Thompson-Horwitz CV, and SDPA

Sample	Analyte	Numeric Results Reported*	Assigned Value (mg/kg)	Between-Laboratory CV* (%)	Thompson-Horwitz CV* (%)	SDPA (as PCV, %)
S1	Abamectin	6	0.0235**	31	22	Not Set
S1	Acephate	9	0.0470	21	22	15
S1	Buprofezin	13	0.76	20	17	15
S1	Endosulfan Sulfate	14	0.0366	22	22	15
S1	Fenvalerate	13	0.0536	25	22	15
S1	Imidacloprid	11	0.0209	15	22	15
S1	Indoxacarb	13	0.256	24	20	15
S1	Methomyl	11	0.442	23	18	15
S2	Bifenthrin	13	0.0169**	37	22	Not Set
S2	Chlorpyrifos	15	0.0292	25	22	15
S2	Cyprodinil	9	0.0568	14	22	15
S2	Dimethoate	13	0.513	20	18	15
S2	Imidacloprid	10	0.0213	17	22	15
S2	Maldison	15	1.69	28	15	15
S2	Methomyl	10	0.68	19	17	15
S2	Phosmet	7	3.4**	39	13	Not Set
S2	Thiometon	4	0.42**	31	18	Not Set
S3	AMPA	6	2.16**	45	14	Not Set
S3	Azoxystrobin	8	0.82	17	16	20
S3	Chlordane	8	0.144	28	21	20
S3	Cypermethrin	9	1.83**	39	15	Not Set
S3	Diazinon	11	0.813	15	17	20
S3	Difenoconazole	7	0.133	19	22	20
S3	Indoxacarb	6	0.289	23	19	20
S3	Maldison	10	1.65	25	15	20
S3	Profenofos	10	0.168	27	21	20
S4	Maleic Hydrazide	4	2.0**	79	14	Not Set

*Values exclude outliers if applicable. **Robust average or median value as applicable (assigned value not set).

To account for possible low bias in the consensus value due to laboratories using inefficient analytical or extraction techniques, two *z*-scores were adjusted for Sample S1 methomyl. A maximum acceptable result was set as the spiked value plus two SDPAs of the spiked value. Results lower than the maximum acceptable result but with a *z*-score greater than 2.0 had their *z*-score adjusted to 2.0. This ensured that any participants reporting results close to the spiked value were not penalised. *z*-Scores for results greater than the maximum acceptable result, and *z*-scores less than 2.0, were left unaltered.

Of 220 results for which *z*-scores were calculated, 194 (88%) returned $|z| \leq 2.0$, indicating an acceptable performance.

Laboratories 4, 5, 6, 9, and 12 reported numeric results for all 20 scored analytes across all three samples. Laboratory 4 achieved acceptable *z*-scores for all analytes.

Laboratory 17 reported results for Sample S1 only, and returned acceptable *z*-scores for all seven scored analytes in this sample.

Three other participants received acceptable *z*-scores for all scored analytes that they reported results for: 3 (11), 14 (6) and 13 (5).

The dispersal of participants' *z*-scores is presented graphically by laboratory in Figure 29; some participants' results were biased high or low for the majority of their results (as circled). The dispersal of participants' z-scores by analyte is presented graphically in Figure 30.

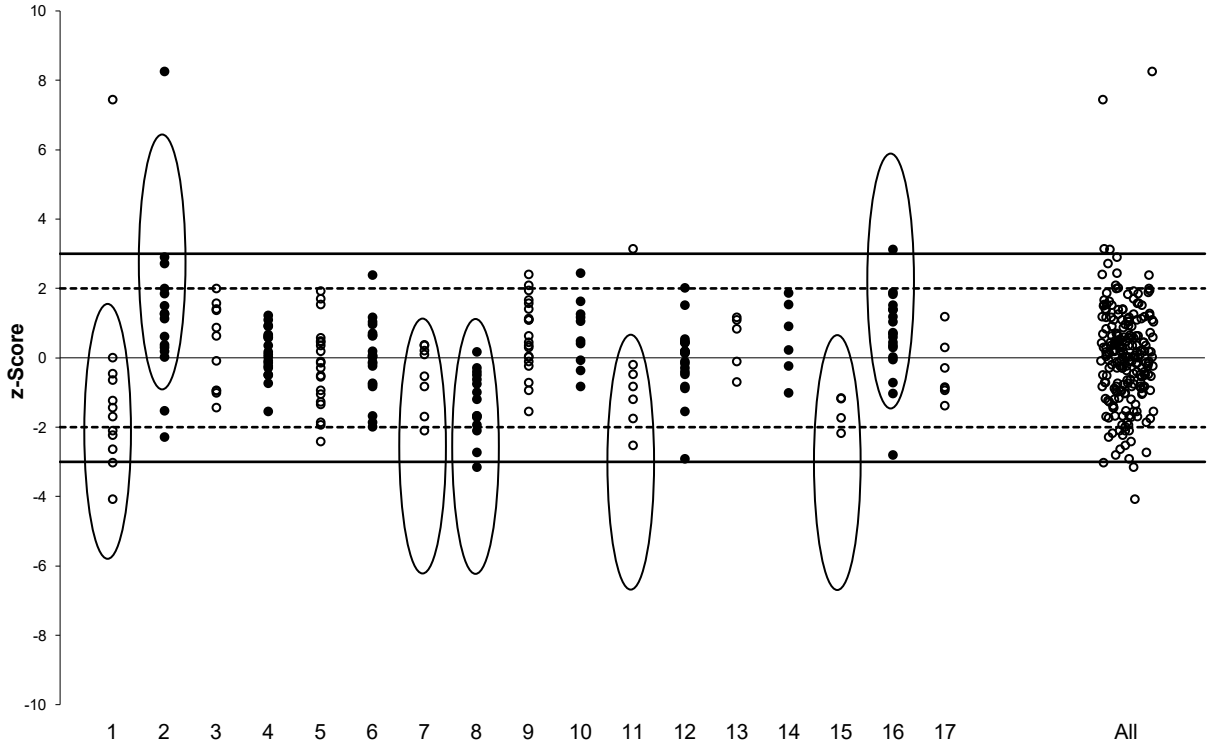


Figure 29 *z*-Score Dispersal by Laboratory

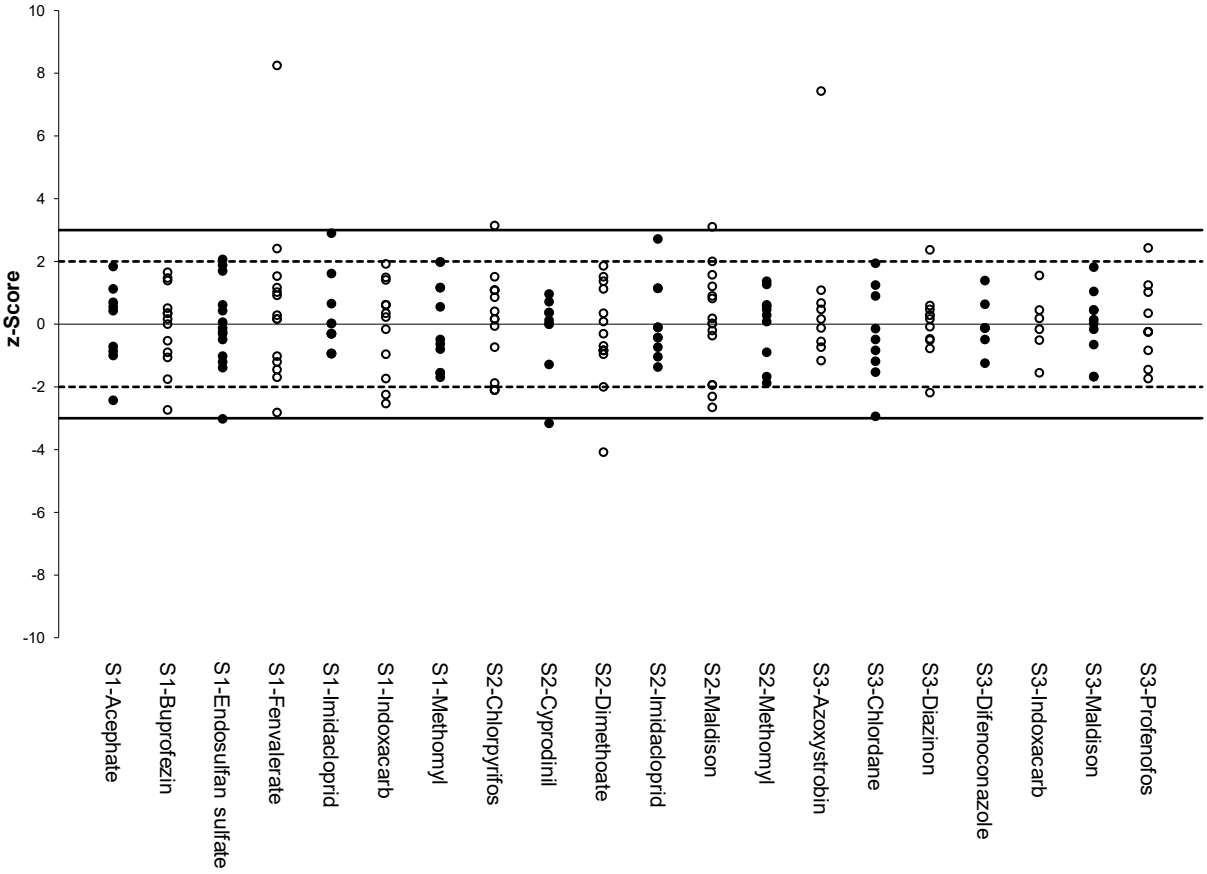


Figure 30 *z*-Score Dispersal by Analyte

6.4 E_n-Scores

The E_n-score indicates how closely a result agrees with the assigned value taking into consideration the respective uncertainties. E_n-scores can be interpreted in conjunction with *z*-scores, as an unacceptable E_n-score can either be caused by issues with measurement, an inappropriate evaluation of measurement 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 218 results for which E_n-scores were calculated, 181 (83%) returned $|E_n| < 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratories 4 and 9 achieved acceptable E_n-scores for all 20 scored analytes in this study.

Laboratory 17 reported results for Sample S1 only, and returned acceptable E_n-scores for all seven scored analytes in this sample.

Three other participants received acceptable *z*-scores for all scored analytes that they reported results for: 10 (10), 14 (6) and 13 (5).

The dispersal of participants' E_n-scores is presented graphically by laboratory in Figure 31.

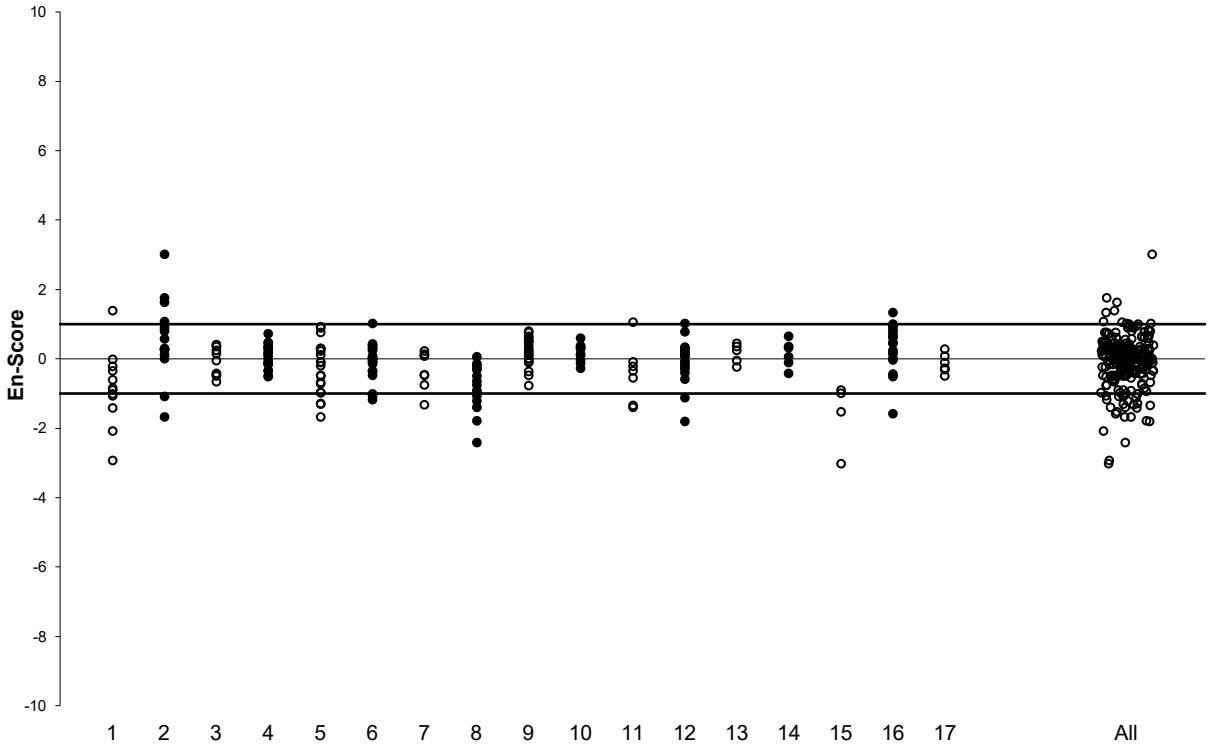


Figure 31 E_n-Score Dispersal by Laboratory

6.5 Range of Pesticides Analysed by Participants

Participants were given a list of analytes that could have been spiked into the samples (Table 2). Of these, 23 different analytes were spiked into the study samples (including maleic hydrazide in pilot Sample S4). Participants were not required to test for all analytes; they had the option to report 'NT' (for 'Not Tested') for pesticides they did not test for.

Laboratories 5 and 12 reported that they tested for all analytes assessed in this study.

Bifenthrin, chlorpyrifos, dimethoate, endosulfan sulfate, fenvalerate, and maldison were the most popular analytes tested for by participants in this study.

6.6 False Negatives

Table 35 presents false negative results. These are analytes present in the samples which a participant tested for but did not report a numeric result; for example, participants reporting a 'less than' result ($< x$) when the assigned value was higher than their limit of reporting (LOR), or participants that did not report anything.

For analytes where no assigned value was set, results have only been considered to be false negatives where the robust average and spiked value were significantly higher than the participants' LOR (i.e. the robust average minus the expanded uncertainty, and the spiked value minus the expanded uncertainty, were both greater than the LOR), or if no value was reported.

Table 35 False Negatives

Lab. Code	Sample	Analyte	Assigned Value (mg/kg)	Spiked Value (mg/kg)	Result* (mg/kg)
1	S3	Indoxacarb	0.289	0.307	NR
2	S3	Azoxystrobin	0.82	0.892	NR
2	S3	Difenoconazole	0.133	0.150	NR

Lab. Code	Sample	Analyte	Assigned Value (mg/kg)	Spiked Value (mg/kg)	Result* (mg/kg)
2	S3	Indoxacarb	0.289	0.307	NR
4	S1	Abamectin	0.0235**	0.0305	NR***
7	S1	Fenvalerate	0.0536	0.0607	<0.05
8	S2	Dimethoate	0.513	0.497	<0.01
8	S3	Profenofos	0.168	0.198	<0.1
10	S1	Fenvalerate	0.0536	0.0607	< 0.05
15	S3	Maldison	1.65	1.95	<1
16	S2	Phosmet	3.4**	3.98	NR
16	S3	Chlordane	0.144	0.199	NR
16	S3	Cypermethrin	1.83**	2.01	NR

*Results reported as NR may or may not be false negatives, depending on the participant's actual LOR. **Robust average or median value (assigned value not set). ***After the release of the Interim Report, Laboratory **4** reported that they had not tested for S1 abamectin; if their result had been reported as NT instead of NR, then this result would not be a false negative.

6.7 Reporting of Additional Analytes

Table 36 presents additional analytes reported by participants that were not spiked into the test samples by the study coordinator.

Table 36 Additional Analytes

Lab. Code	Sample	Analyte	Result (mg/kg)	Uncertainty (mg/kg)	Recovery (%)
5	S3	Glyphosate	0.026	0.0078	NR
8	S2	Azinphos-methyl	2.3	0.69	78

6.8 Summary of Participants' Results and Performances

Summaries of participants' results and performances for scored analytes in this PT study are presented in Tables 37 to 39, and Figure 32.

Table 37 Summary of Participants' Sample S1 Results*

Lab. Code	Acephate	Buprofezin	Endosulfan sulfate	Fenvalerate	Imidacloprid	Indoxacarb	Methomyl
AV	0.0470	0.76	0.0366	0.0536	0.0209	0.256	0.442
1	NT	0.76	0.02	0.04	NT	0.17	NT
2	0.06	0.93	0.04	0.12	0.03	NT	0.61
3	NT	0.92	0.031	0.042	0.018	0.28	0.65
4	0.051	0.8	0.035	0.061	0.023	0.28	0.34
5	0.03	0.64	0.046	0.066	0.018	0.33	0.48
6	0.052	0.78	0.037	0.062	0.021	0.28	0.39
7	NT	0.70	NT	<0.05	NT	0.27	0.33
8	0.04	0.45	0.03	0.055	0.02	0.19	0.40
9	0.055	0.95	0.048	0.073	0.018	0.31	0.34
10	NT	NT	< 0.05	< 0.05	0.026	NT	NT
11	NT	0.560	0.034	0.044	NT	0.159	NT
12	0.050	0.82	0.039	0.055	0.020	0.25	0.41
13	NT	NT	0.036	0.063	NT	NT	NT
14	NT	NT	0.0353	0.0455	NT	0.265	NT
15	NS	NS	NS	NS	NS	NS	NS
16	0.042	0.801	0.047	0.031	0.021	0.314	0.52
17	0.041	0.66	0.029	0.056	0.020	0.22	0.52

*All results are mg/kg. Shaded cells are results which returned a questionable or not acceptable *z*-score. AV = Assigned Value.

Table 38 Summary of Participants' Sample S2 Results*

Lab. Code	Chlorpyrifos	Cyprodinil	Dimethoate	Imidacloprid	Maldison	Methomyl
AV	0.0292	0.0568	0.513	0.0213	1.69	0.68
1	0.02	NT	0.2	NT	1.02	NT
2	0.03	0.06	0.6	0.03	1.11	0.81
3	0.033	NT	0.44	0.021	2.09	0.82
4	0.034	0.057	0.52	0.021	2.0	0.74
5	0.021	0.046	0.49	0.017	1.2	0.73
6	0.026	0.065	0.36	0.025	1.7	0.49
7	0.02	0.06	0.45	NT	1.74	0.69
8	0.02	0.03	<0.01	0.02	1.2	0.51
9	0.034	0.057	0.54	0.019	1.7	0.744
10	0.031	NT	0.45	0.025	1.6	NT
11	0.043	NT	0.45	NT	1.64	NT
12	0.030	0.058	0.63	0.020	2.20	0.59
13	0.034	NT	0.46	NT	1.9	NT
14	0.0359	NT	0.657	NT	1.92	NT
15	NS	NS	NS	NS	NS	NS
16	0.029	0.063	0.619	0.018	2.48	0.711
17	NS	NS	NS	NS	NS	NS

*All results are mg/kg. Shaded cells are results which returned a questionable or not acceptable z-score. AV = Assigned Value.

Table 39 Summary of Participants' Sample S3 Results*

Lab. Code	Azoxystrobin	Chlordane	Diazinon	Difenoconazole	Indoxacarb	Maldison	Profenofos
AV	0.82	0.144	0.813	0.133	0.289	1.65	0.168
1	2.04	NT	0.74	0.1	NR	1.44	0.12
2	NR	0.1	0.86	NR	NR	1.66	0.21
3	NS	NS	NS	NS	NS	NS	NS
4	0.7	0.17	0.84	0.12	0.26	1.6	0.16
5	0.73	0.14	0.73	0.13	0.3	1.8	0.18
6	0.80	0.12	1.2	0.15	0.28	1.1	0.16
7	NT	NT	NT	NT	NT	NT	NT
8	NT	0.13	0.69	NT	NT	1.1	<0.1
9	1.0	0.20	0.86	0.13	0.38	1.8	0.16
10	0.9	0.18	0.8	NT	NT	2.0	0.25
11	NS	NS	NS	NS	NS	NS	NS
12	0.85	0.060	0.89	0.13	0.20	1.70	0.14
13	NS	NS	NS	NS	NS	NS	NS
14	NS	NS	NS	NS	NS	NS	NS
15	0.63	0.11	0.46	NT	NT	<1	0.11
16	0.931	NR	0.911	0.17	0.315	2.254	0.203
17	NS	NS	NS	NS	NS	NS	NS

*All results are mg/kg. Shaded cells are results which returned a questionable or not acceptable z-score. AV = Assigned Value.

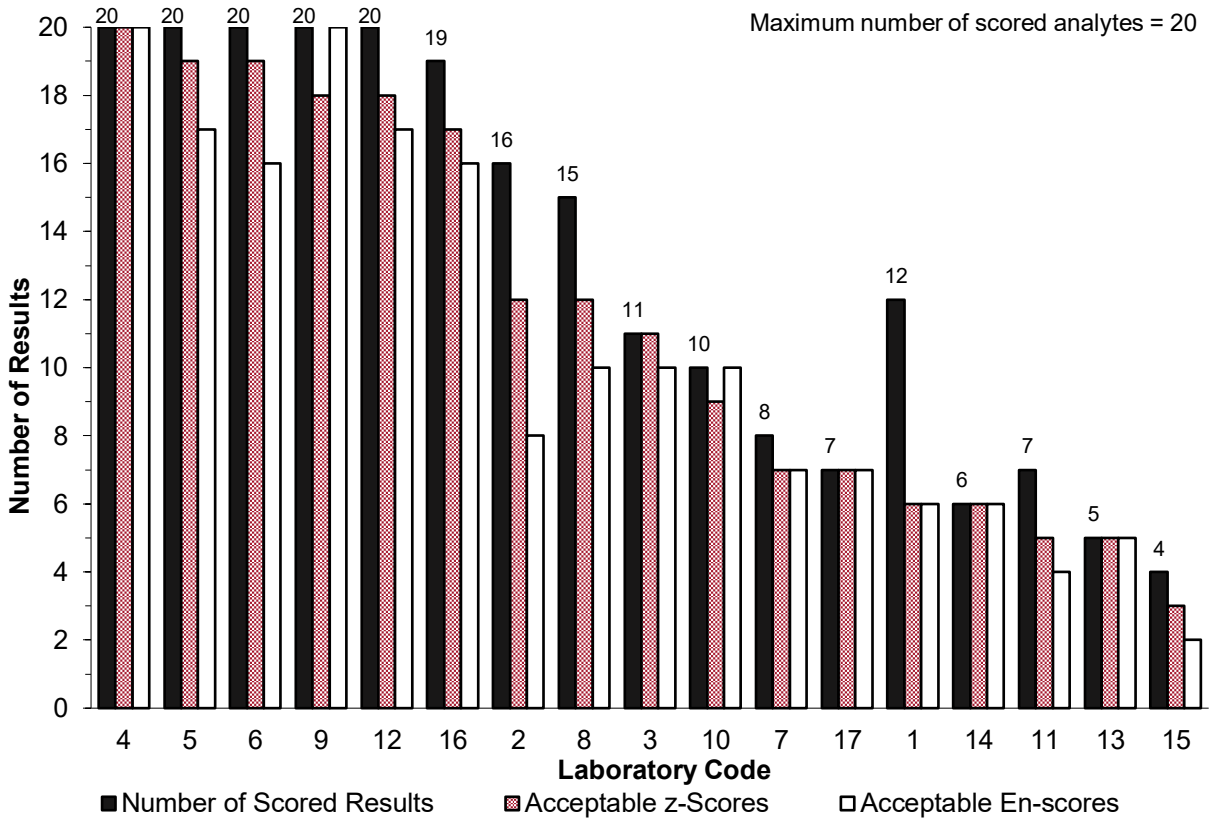


Figure 32 Summary of Participants' Performance

6.9 Participants' Results and Analytical Methods

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 of surrogates or not, according to their standard procedure. Results reported in this way reflect the true variability of results reported by laboratories to clients.

Participants were also provided with unspiked samples to be analysed if part of their routine procedures, however, were instructed not to correct the spiked sample results for any analytes detected in the unspiked samples. All participants except for Laboratory 6 reported analysing the unspiked samples.

Samples S1, S2, and S3

Sample S1 was tomato puree, Sample S2 was fruit puree while Sample S3 was hemp flour.

This was the first NMIA pesticides in food study to contain a dry powder matrix (Sample S3 hemp flour). This sample was introduced in response to participants' requests for a pesticides in cannabis PT study, with hemp flour selected as a representative cannabis-like matrix. The variability of participant's results, as well as recovery of the spiked value, were similar to that observed for moist (puree) food matrices.

A variety of analytical methods were used by participants in this study (Appendix 4). Most participants used the same method for each analyte across the different samples, however there were a few cases where participants used a different method depending on the sample.

Plots of participants' performance in the three study samples versus the amount of sample taken for analysis are presented in Figure 33. Laboratories used a wide range of sample sizes, 5 g to 20 g for Samples S1 and S2, and 0.5 g to 20 g for Sample S3. There was no significant trend observed between participants' performance and the sample amount used for analysis.

All participants except for Laboratory 5 reported recoveries for at least one analyte in this study, and the recoveries reported were within the range of 46% to 254%. Some participants in this study applied recovery correction (Laboratories 2, 5, 6, 9, 14, and 15), however, for a subset of these participants their results remained biased (Figure 29).

Participants were asked to report if they used internal standards as part of their analysis (Figure 34). No significant trend observed was observed between the participants' performance and the use of internal standards.

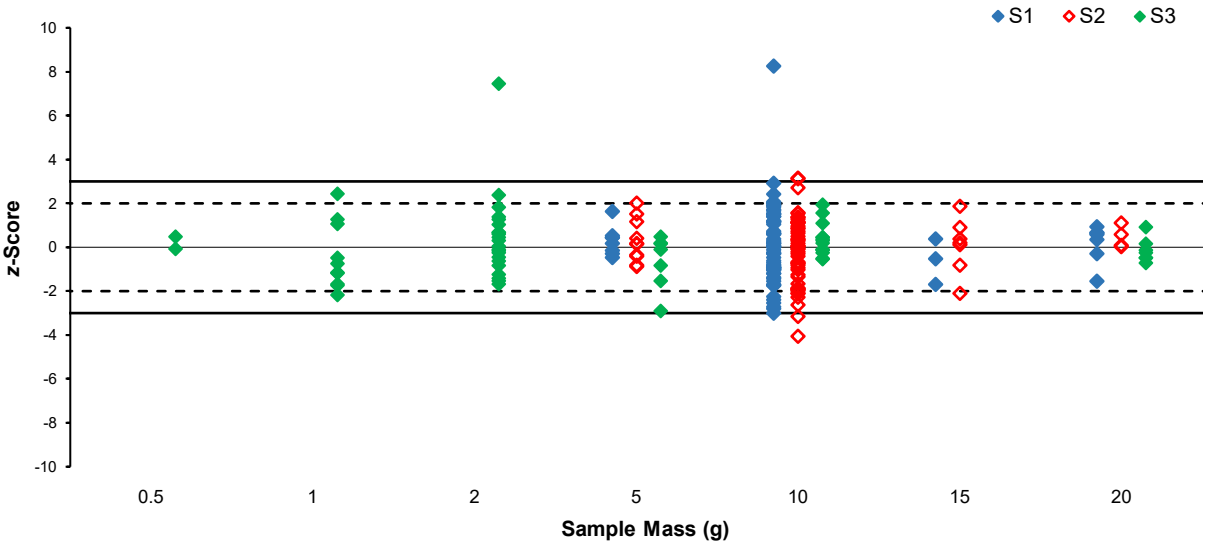


Figure 33 *z*-Score vs Sample Mass Used for Analysis

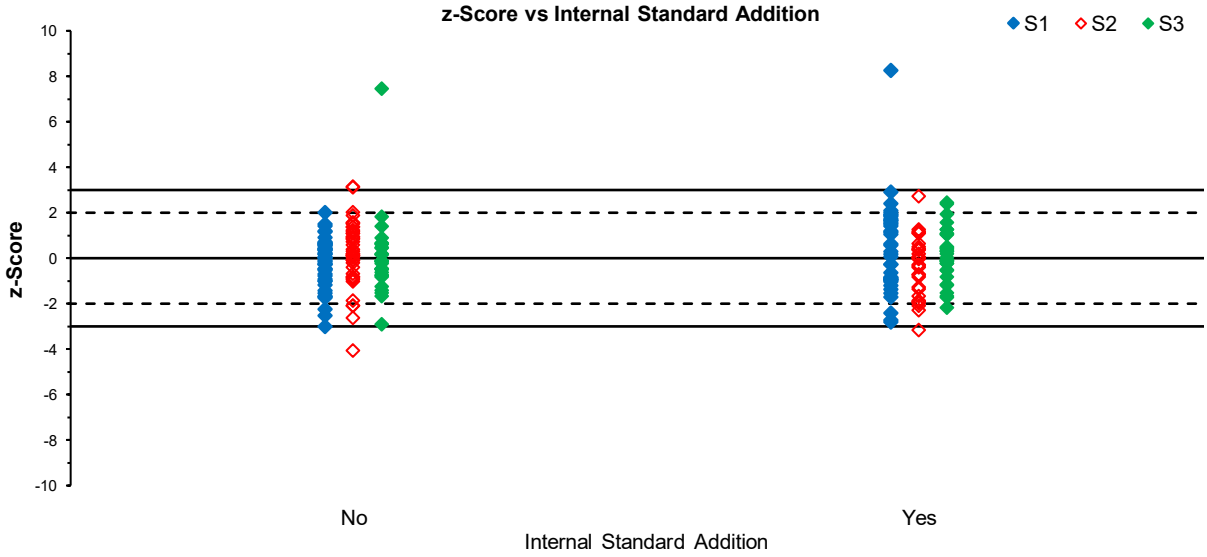


Figure 34 *z*-Score vs Use of Internal Standard

The most common methodology used in this study was based on the QuEChERS procedure.[11] Some participants clarified that they used solid-liquid extraction with mechanical agitation (SLE (MA)) as their initial extraction step before performing QuEChERS dispersive SPE (dSPE) clean-up. The most common extraction solvent was acetonitrile (ACN). Most participants analysed extracts on gas chromatography (GC) or liquid chromatography (LC) coupled to mass spectrometry (MS) or tandem mass spectrometry (MS/MS), though some participants used other detectors such as electron capture detection (ECD) or flame photometric detection (FPD).

Individual Analyte Commentary – Samples S1, S2, and S3

Abamectin Five of the six results reported for abamectin in Sample S1 (Laboratories 8, 9, 12, 16, and 17) were in good agreement with each other and the spiked level. Laboratory 5's result was biased low. This participant used LC-MS instead of LC-MS/MS (Figure 35); matrix effects amplified on LC-MS may have contributed to the underestimation of the analyte level.

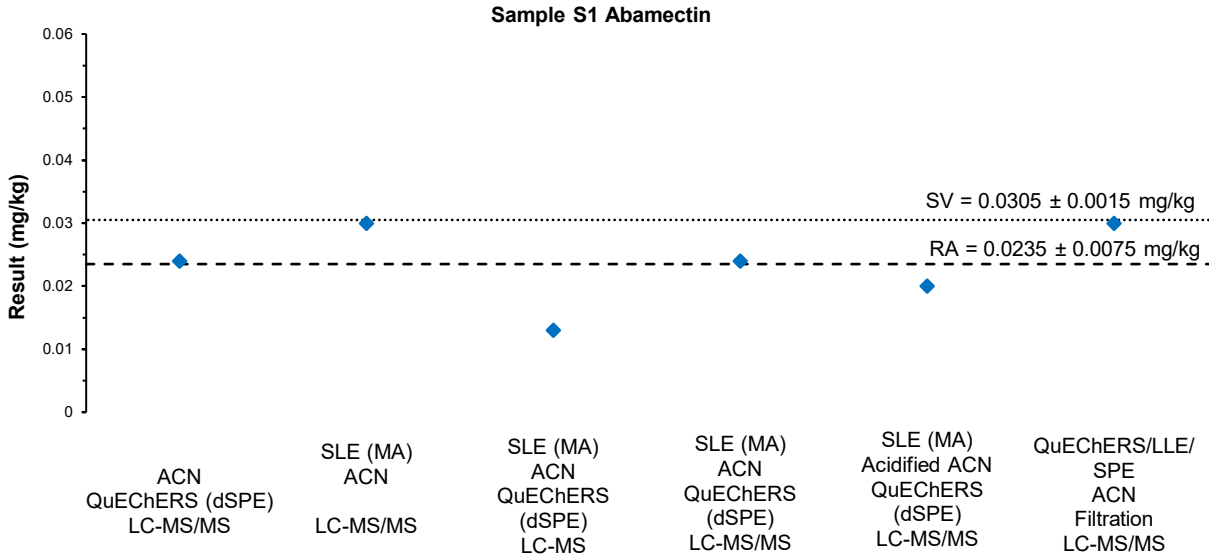


Figure 35 Sample S1 Abamectin Result vs Methodology

Acephate results in Sample S1 were generally in good agreement with each other and the spiked value. As above, Laboratory 5 used LC-MS for analysis and returned a result biased low (Figure 36).

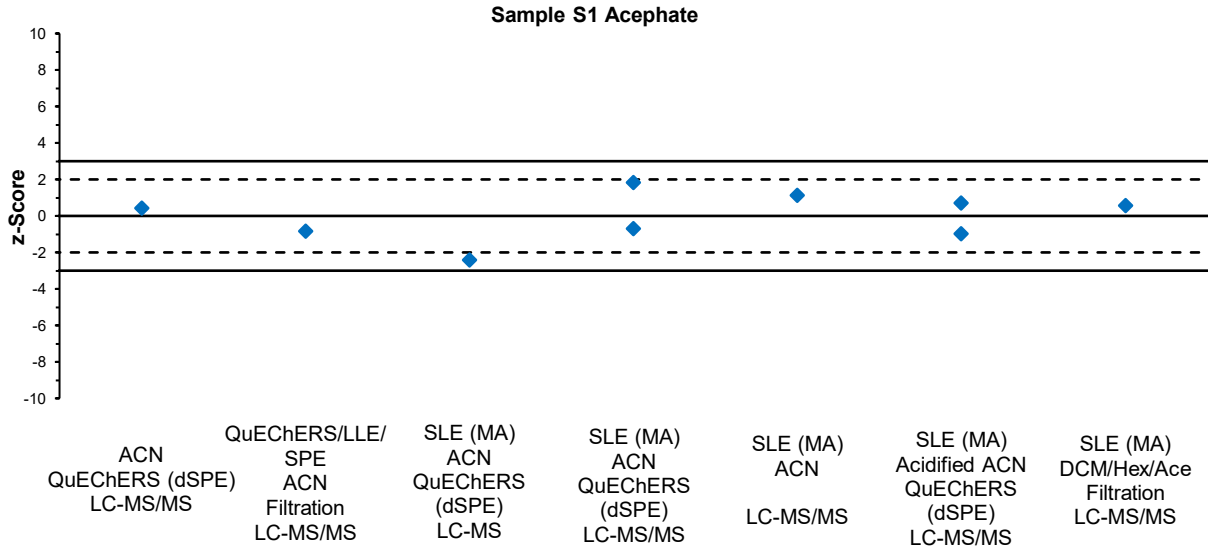


Figure 36 Sample S1 Acephate *z*-Scores vs Methodology

AMPA No assigned value could be set for AMPA in Sample S3. Only six participants reported numeric results for this analyte; the results reported by Laboratories 5, 10, 12, and 15 were in excellent agreement with each other and the spiked value (Figure 37).

Due to the high polarity of AMPA, the methodologies employed by participants for this analyte were generally different compared to the other analytes in this study. Some participants followed the QuPPe procedure,[12] and most participants used methanol and/or

aqueous extraction solvents instead. One participant used SLE with sonication (SLE (S)) instead of mechanical agitation. The participants who recovered the lowest proportion of the spiked analyte were those who used methanol only or basified methanol as extraction reagent.

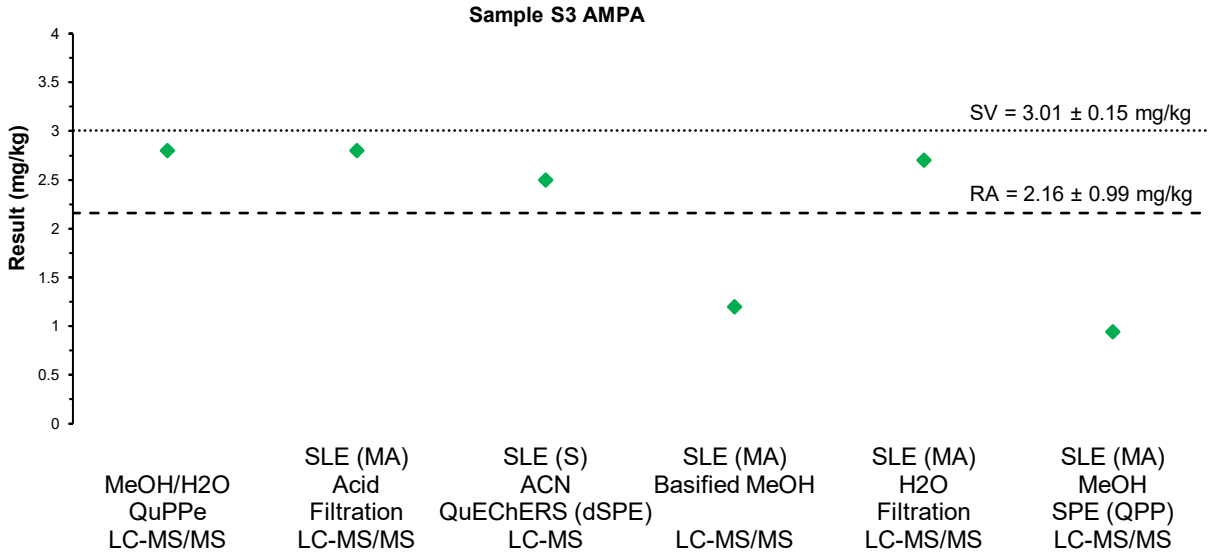


Figure 37 Sample S3 AMPA Results vs Methodology

Azoxystrobin Measurements of azoxystrobin in Sample S3 did not challenge participants analytical techniques (Figure 38). All reported results were in excellent agreement with each other except for one. Laboratory 1 reported a result that was approximately 2.5 times greater than the assigned value; this participant may need to check for method or laboratory bias (e.g. check their standard preparation procedure).

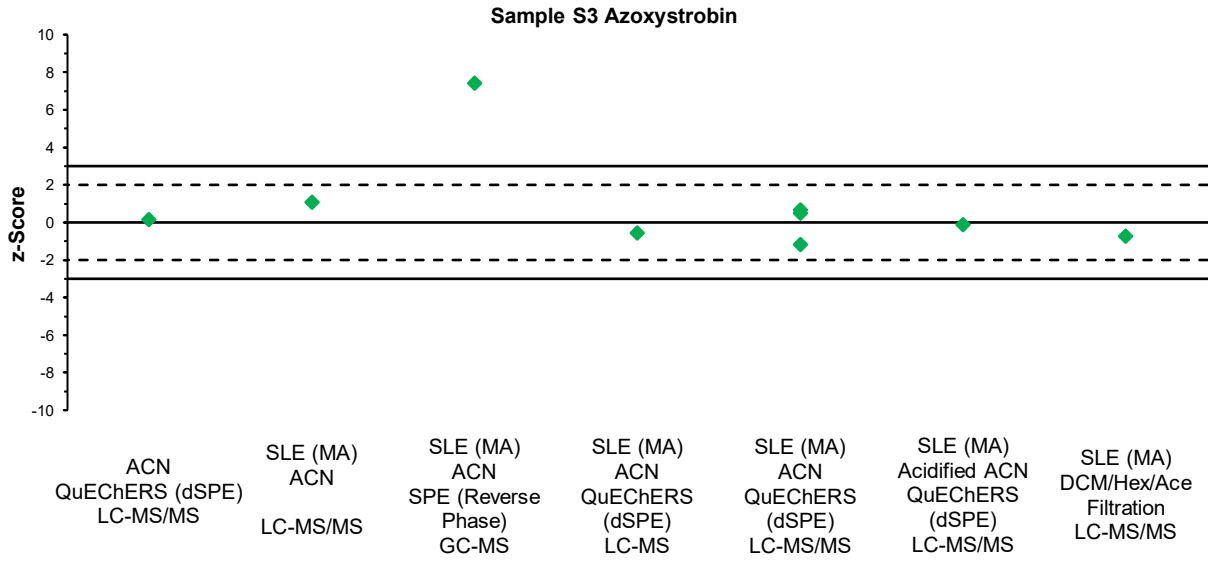


Figure 38 Sample S3 Azoxystrobin *z*-Scores vs Methodology

Bifenthrin was an incurred analyte in Sample S2 blueberry, and no assigned value could be set as reported results were too variable. Most results from participants using GC-MS or GC-ECD were biased low as compared to participants who used GC-MS/MS instead for analysis (Figure 39).

Buprofezin Participants used a variety of methodologies for Sample S1 buprofezin, and these different methodologies generally produced compatible results (Figure 40).

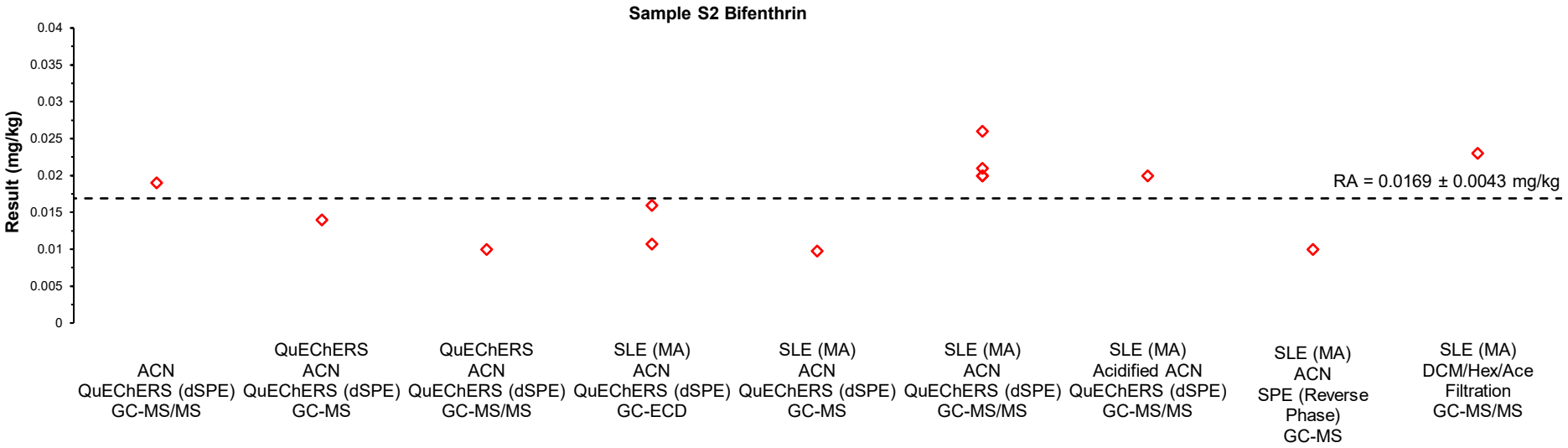


Figure 39 Sample S2 Bifenthrin Results vs Methodology

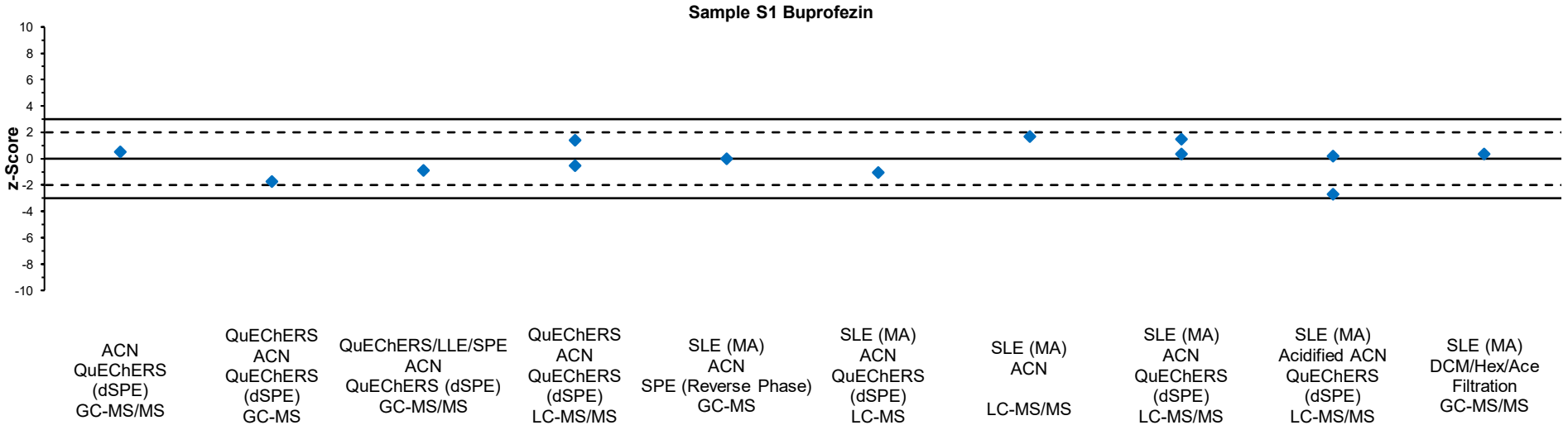


Figure 40 Sample S1 Buprofezin *z*-Scores vs Methodology

Chlordane was spiked into Sample S3 hemp flour. Most methods produced compatible results (Figure 41). Laboratory 12 reported a result that was approximately half of the assigned value; this participant may need to check for method or laboratory bias (e.g. check their standard preparation procedure).

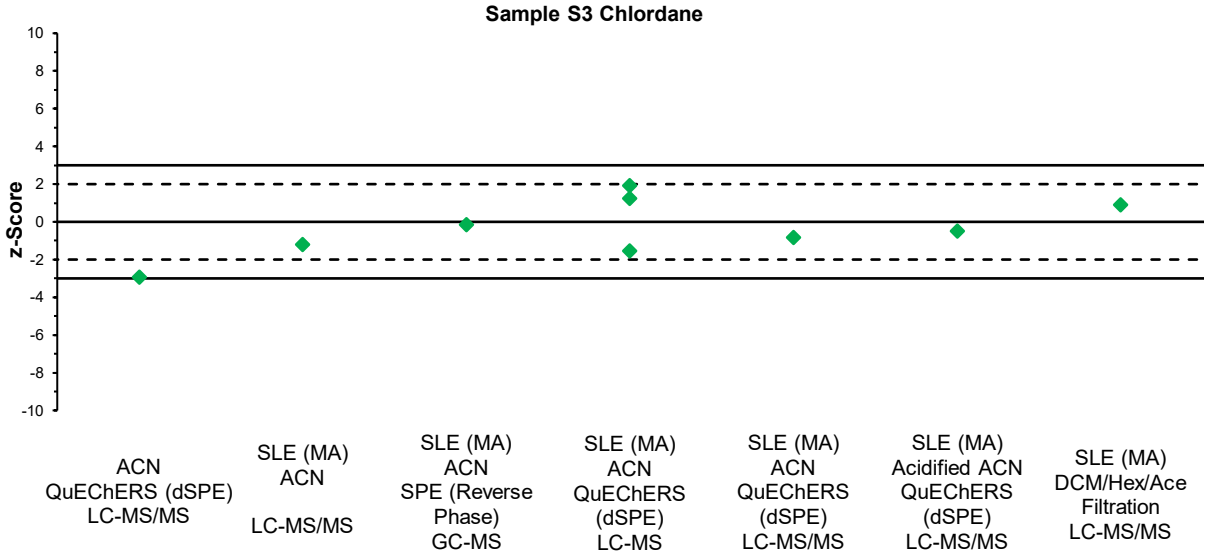
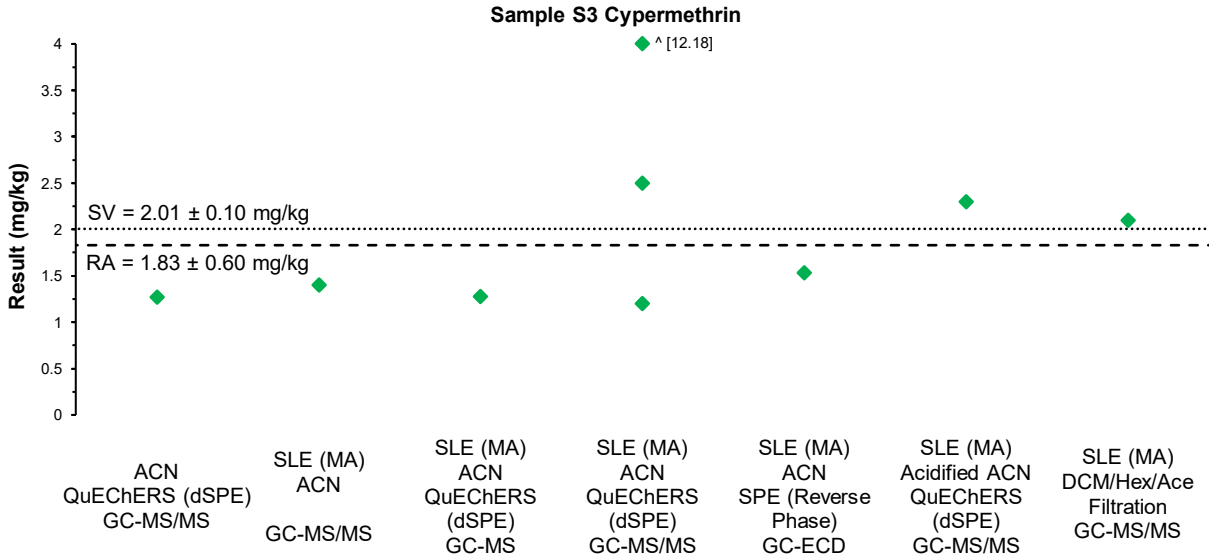


Figure 41 Sample S3 Chlordane *z*-Scores vs Methodology

Chlorpyrifos Most methods produced compatible results for Sample S2 chlorpyrifos (Figure 43). Laboratory 13 was the only participant to use GC-FPD, and their result was biased high.

Cypermethrin was spiked into Sample S3, however no assigned value could be set and there was no clear methodology trend (Figure 42). Laboratory 2 reported a result that was almost 7 times higher than robust average, this participant may need to review their procedure to identify the source of this bias.



^Result has been adjusted to be fit on the chart. The original result is given in the brackets.

Figure 42 Sample S3 Cypermethrin *z*-Scores vs Methodology

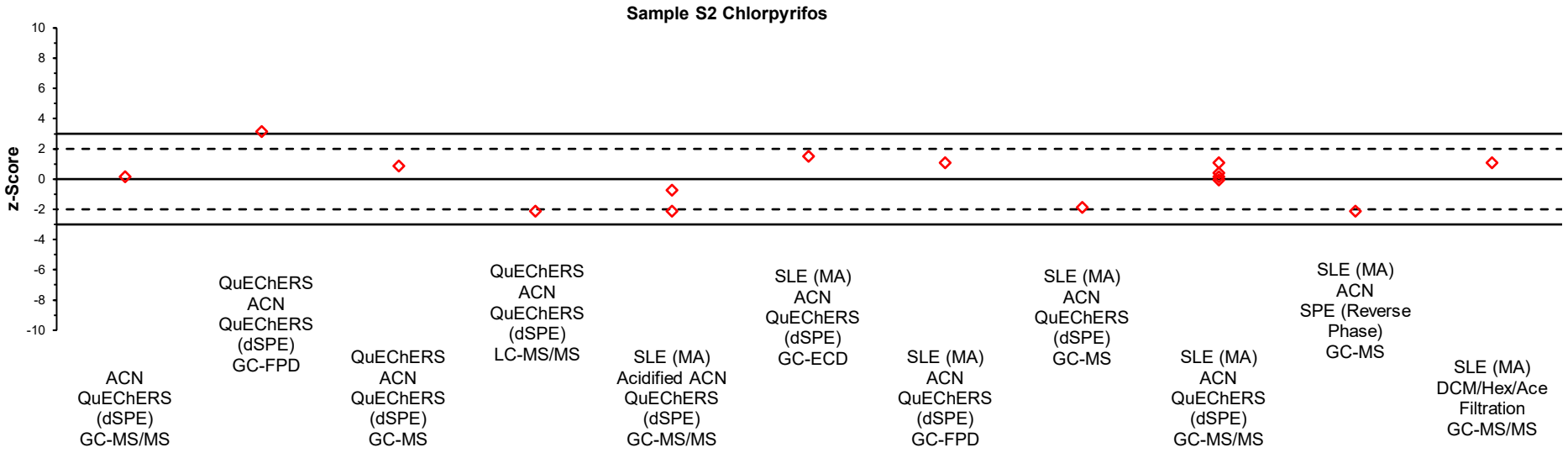


Figure 43 Sample S2 Chlorpyrifos *z*-Scores vs Methodology

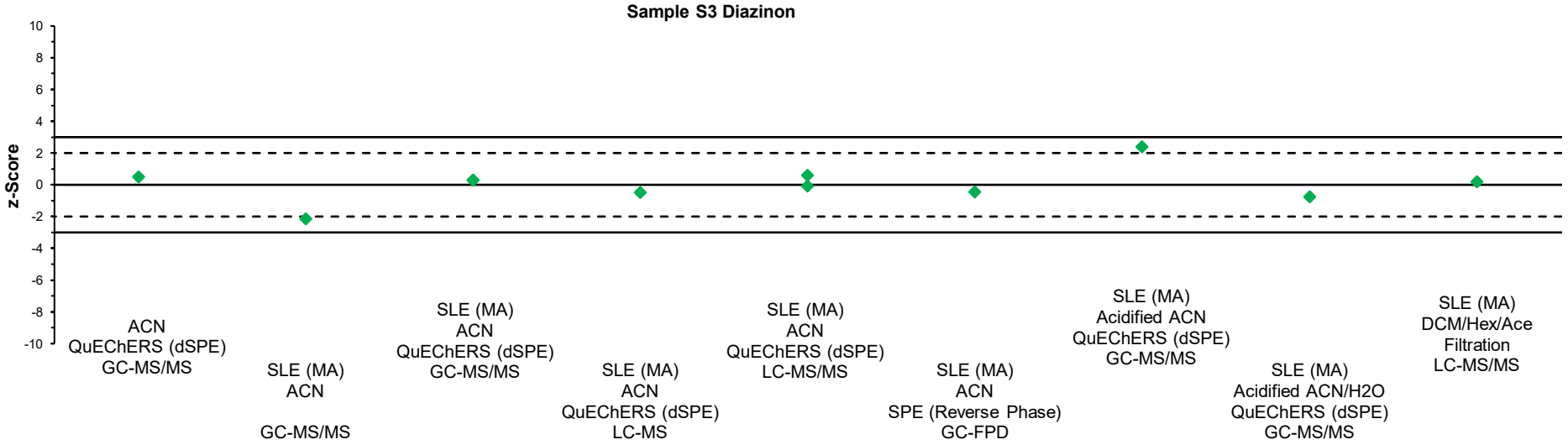


Figure 44 Sample S3 Diazinon *z*-Scores vs Methodology

Cyprodinil Eight of the nine results for Sample S2 cyprodinil were in good agreement with each other and the spiked value (Figure 45). Laboratory 8 was biased low. They reported an extraction time of only one minute; this may have been insufficient for complete extraction of this analyte from the sample.

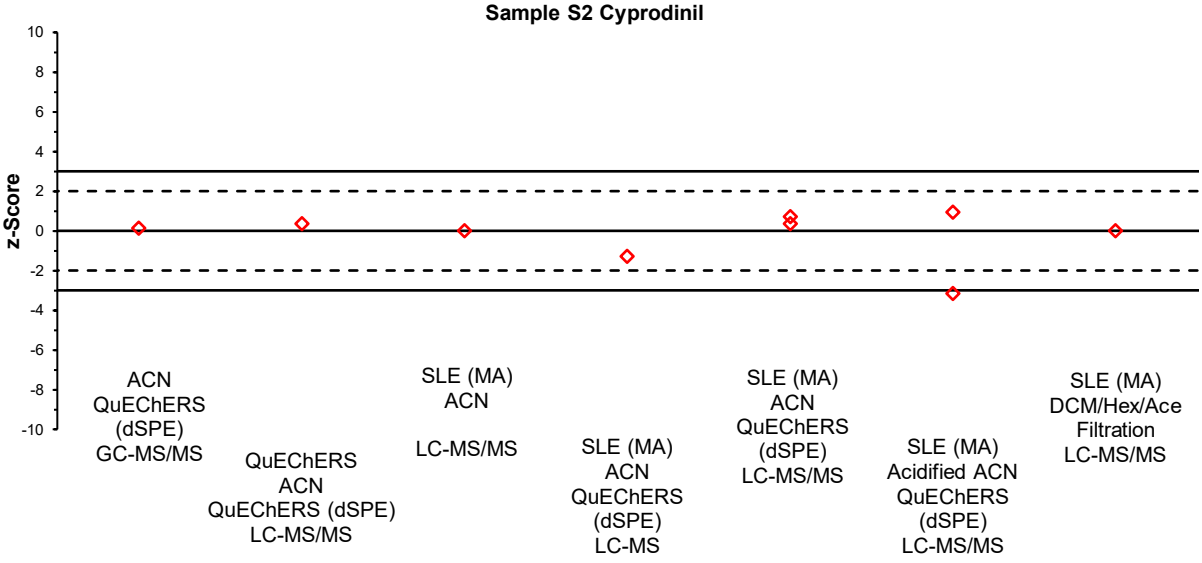


Figure 45 Sample S2 Cyprodinil *z*-Scores vs Methodology

Diazinon Most methodologies used for this analyte produced compatible results (Figure 44).

Difenoconazole was spiked into Sample S3, and all results were in good agreement with each other and the spiked value (Figure 46).

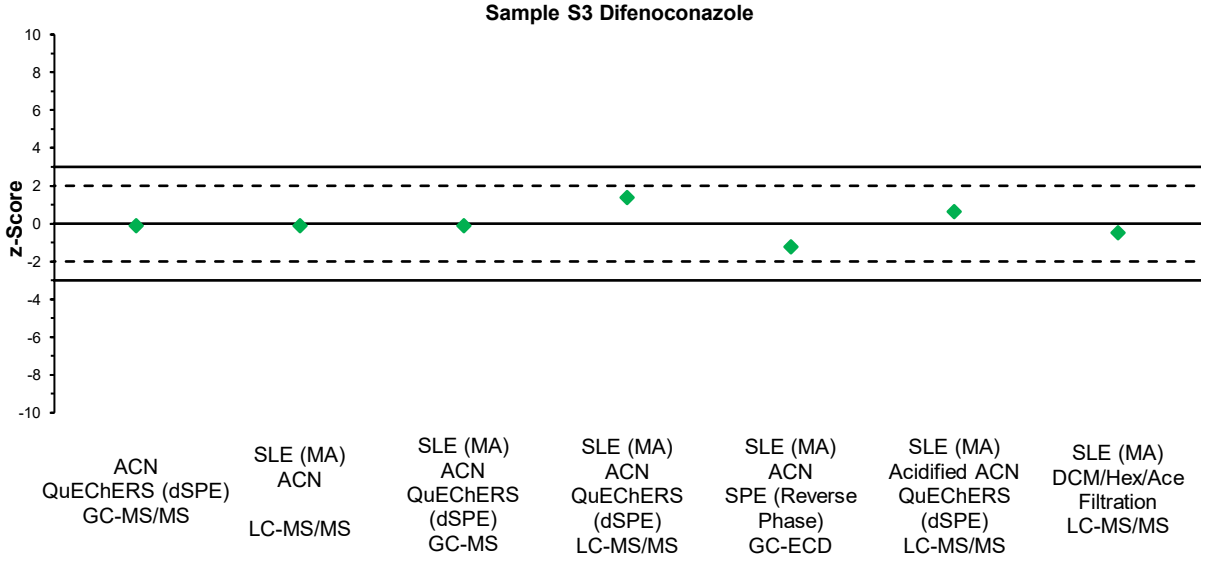


Figure 46 Sample S3 Difenoconazole *z*-Scores vs Methodology

Dimethoate 13 of the 14 reported results for dimethoate in Sample S1 were in good agreement with each other and the spiked value. Laboratory 1 was the only participant to employ a SPE (reverse-phase) clean-up step: their result was biased low (Figure 47).

Endosulfan sulfate results in Sample S1 were also in good agreement with each other and the spiked value. As above, Laboratory 1 was the only participant to employ a SPE (reverse-phase) clean-up step, and this participant returned a result biased low (Figure 48).

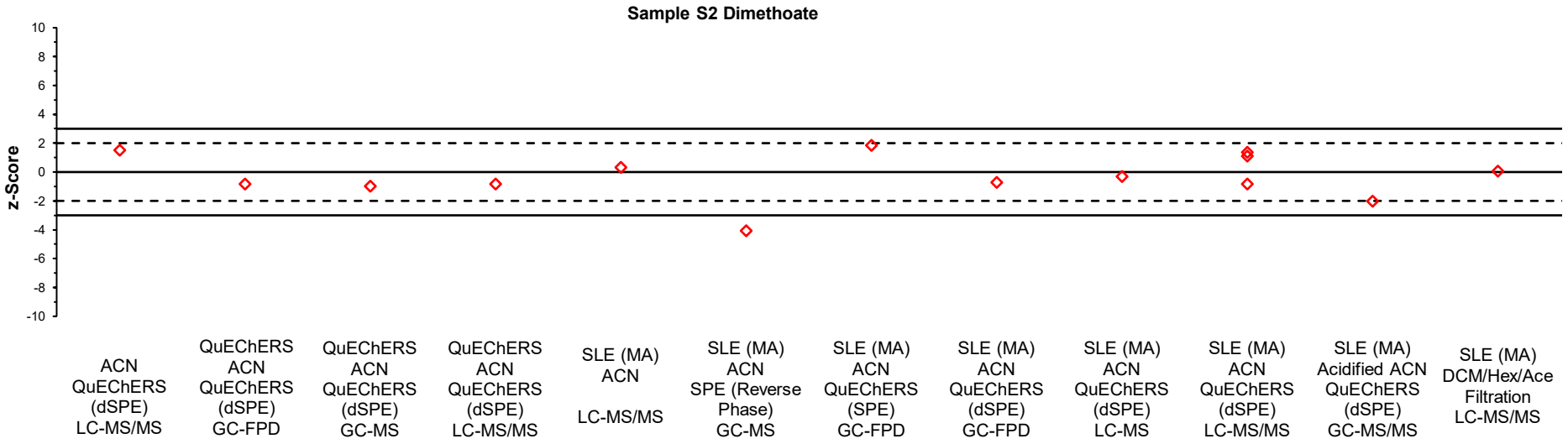


Figure 47 Sample S2 Dimethoate *z*-Scores vs Methodology

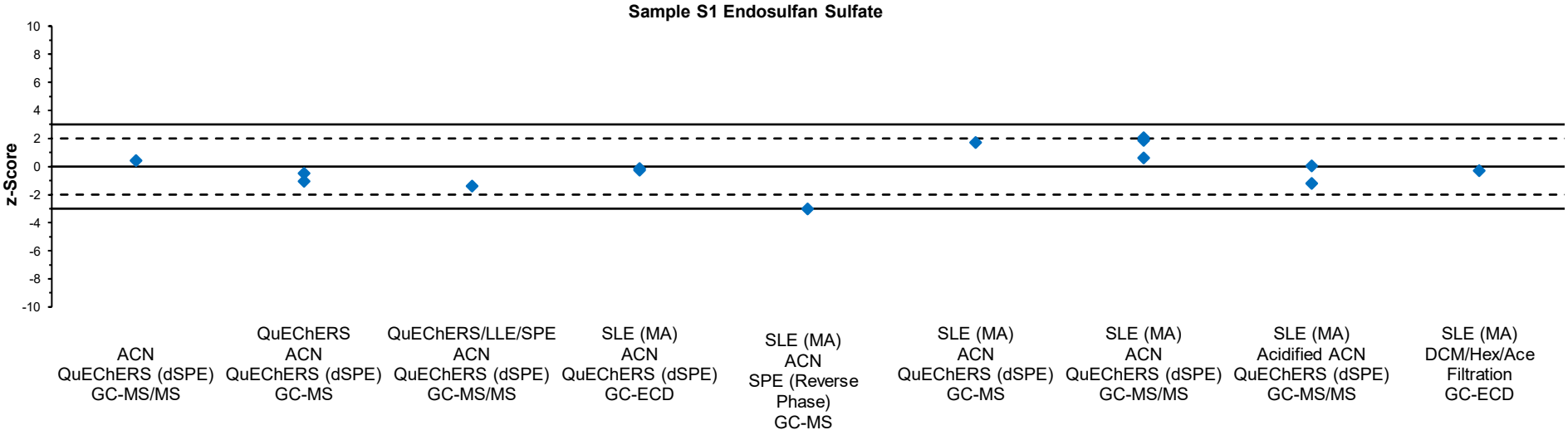


Figure 48 Sample S1 Endosulfan Sulfate *z*-Scores vs Methodology

Fenvalerate Most methods produced compatible results for Sample S1 fenvalerate (Figure 50). Laboratory 2's result was approximately two times the assigned value, this participant may need to check for method or laboratory bias (e.g. check their standard preparation procedure).

Imidacloprid was spiked into both Sample S1 tomato and Sample S2 blueberry, at similar levels. Matrix differences did not affect analyses significantly, with participants using the same method for both samples (where applicable) and performing very similarly across both samples (Figure 51). Laboratory 2's results were consistently around 1.4 times higher than the respective assigned values for Samples S1 and S2, this participant may need to check for method or laboratory bias (e.g. check their standard preparation procedure).

Indoxacarb was present in both Sample S1 tomato and Sample S3 hemp flour. Extraction of this analyte was more efficient in hemp flour (assigned value was 94% of the spiked value) as compared to tomato (assigned value was 85% of the spiked value). Laboratory 4 reported using GC-MS/MS for Sample S1 but LC-MS/MS for Sample S3; all other participants who analysed both samples reported using the same method. All questionable low results were from GC-MS determination (Figure 52).

Maldison was spiked into both Sample S2 blueberry and Sample S3 hemp flour. Participants overall performed similarly for this analyte in both matrices.

Some participants used different methodologies between the two samples for this analyte (Figure 53). Laboratory 1 used GC-MS for Sample S2, and GC-FPD for Sample S3. Laboratory 8 used different extraction solvents: acidified ACN for Sample S2, and acidified ACN/water solution for Sample S3. Laboratory 9 employed a dSPE clean-up for Sample S2, and then analysed with GC-MS/MS, while for Sample S3 this participant did not perform a clean-up and analysed instead on LC-MS/MS. All performed satisfactorily in both matrices regardless of the method employed.

Methomyl was spiked into Sample S1 tomato and Sample S2 blueberry. This analyte was more challenging for participants in tomato as compared to blueberry, with a lower recovery of the spiked value and a higher variability in reported results for Sample S1 as compared to Sample S2, though overall results were in reasonable agreement with each other in both samples. All participants analysing both samples used the same method (Figure 49).

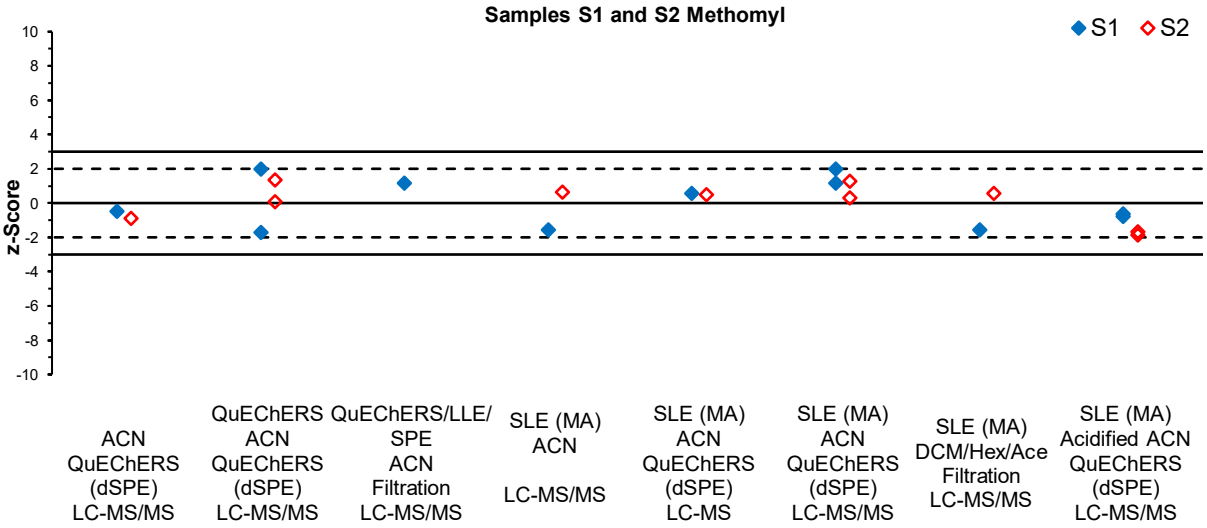


Figure 49 Samples S1 and S2 Methomyl *z*-Scores vs Methodology

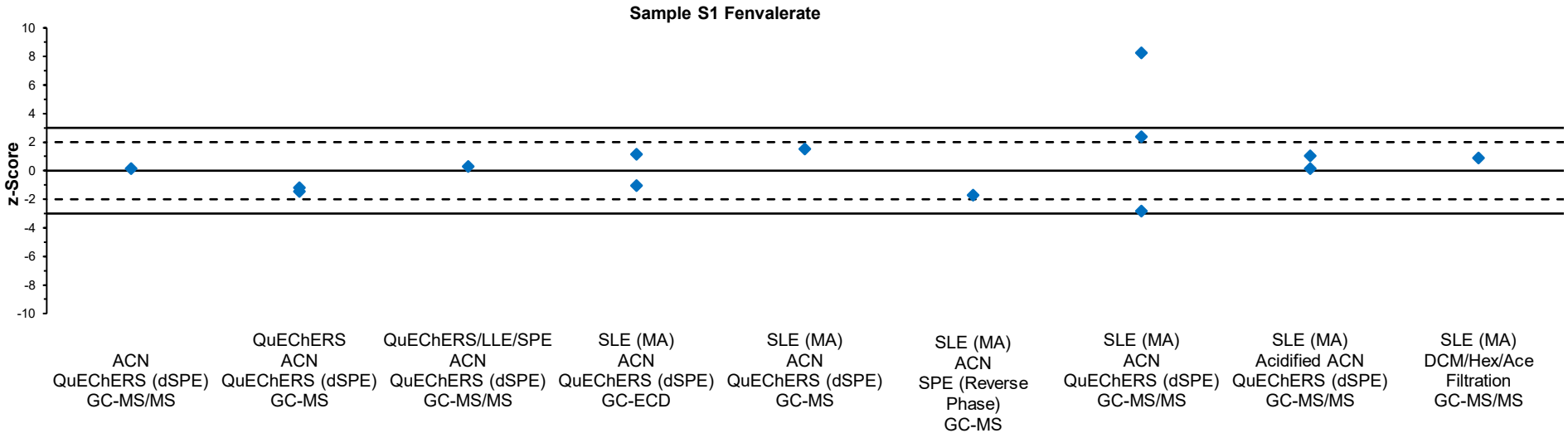


Figure 50 Sample S1 Fenvalerate *z*-Scores vs Methodology

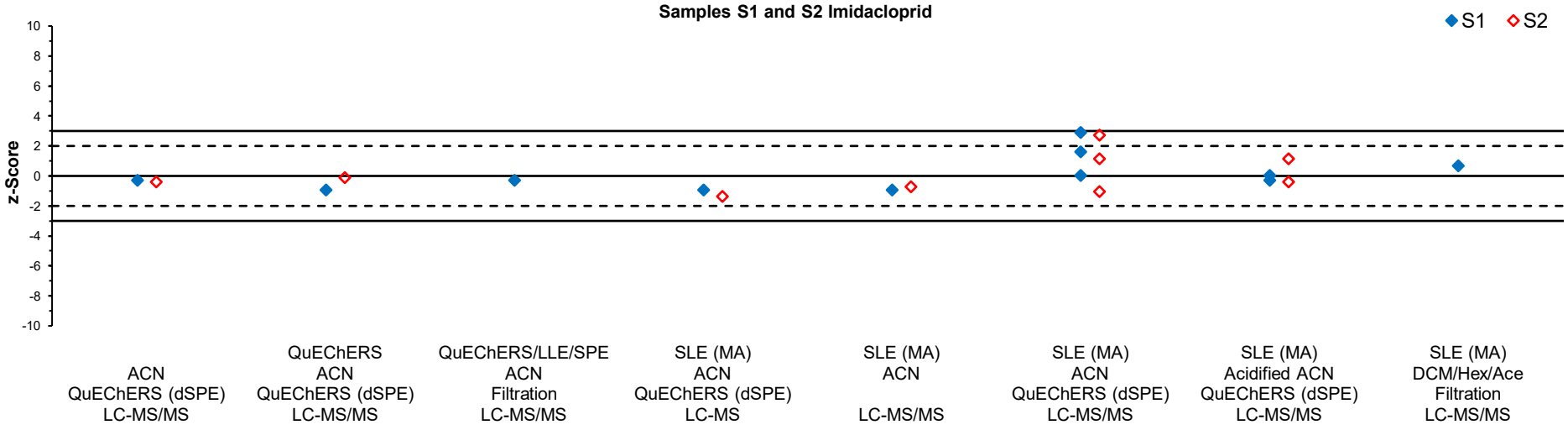


Figure 51 Samples S1 and S2 Imidacloprid *z*-Scores vs Methodology

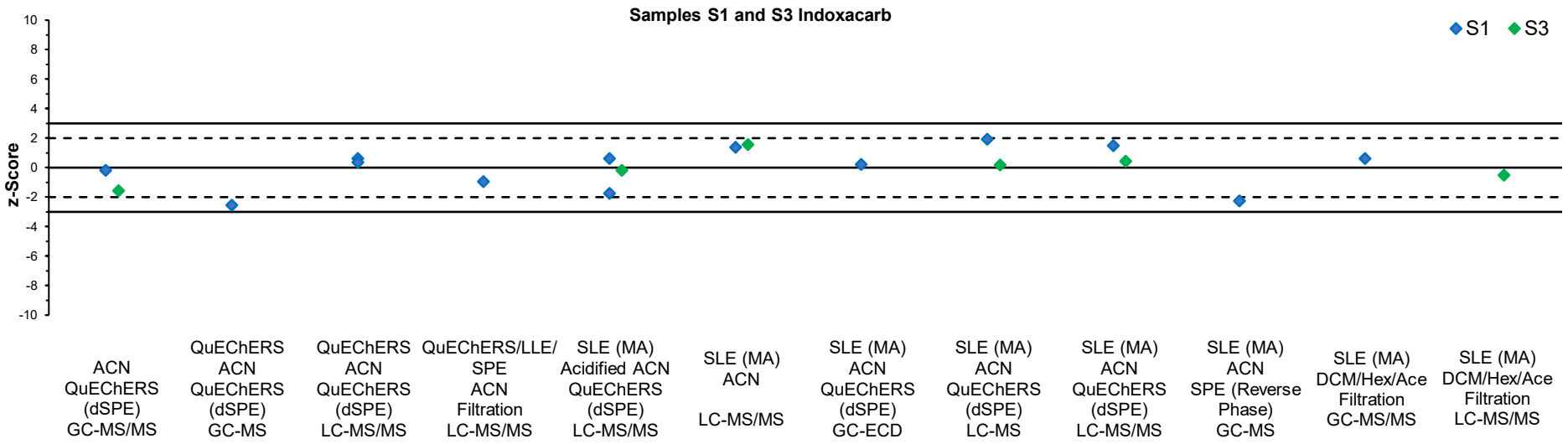


Figure 52 Samples S1 and S3 Indoxacarb *z*-Scores vs Methodology

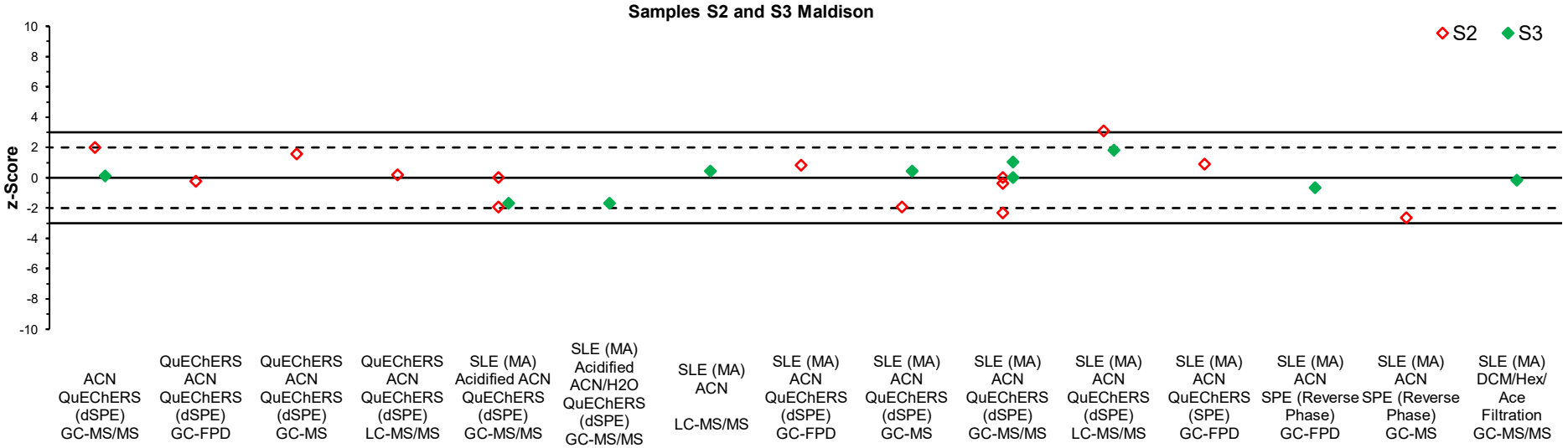


Figure 53 Samples S2 and S3 Maldison *z*-Scores vs Methodology

Phosmet was spiked in Sample S2, however no assigned value could be set. There was a broad distribution of results, however several participants reported results close to the spiked value (Figure 54). Laboratory 8 was biased low. This participant had an extraction time of one minute; this may have been insufficient for complete extraction of this analyte from the sample.

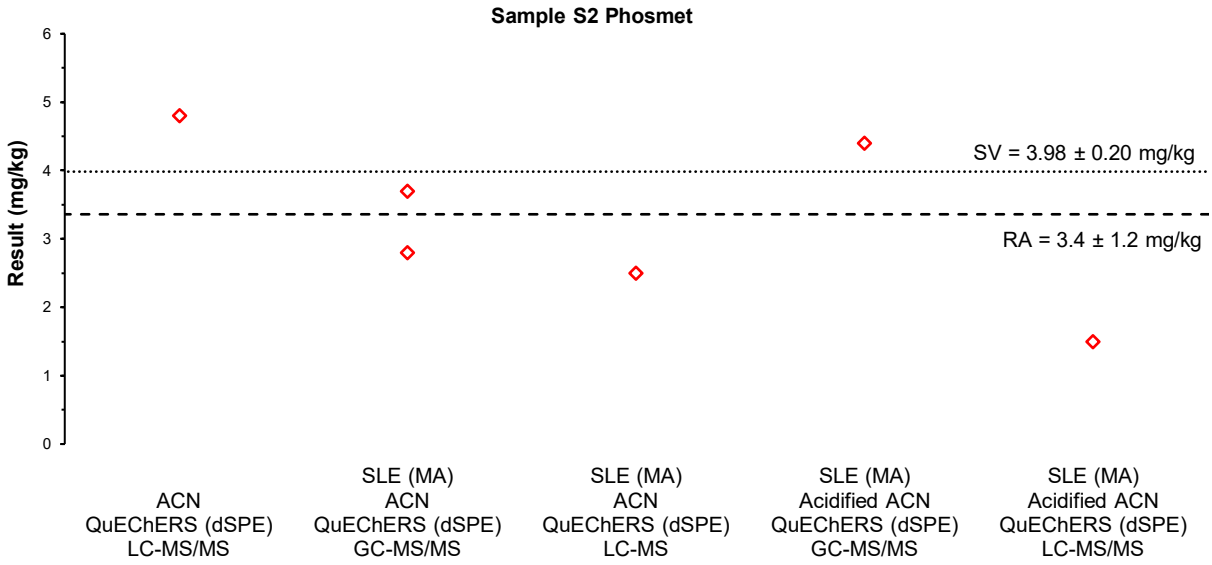


Figure 54 Sample S2 Phosmet Results vs Methodology

Profenofos results were generally compatible with each other regardless of the method used (Figure 55).

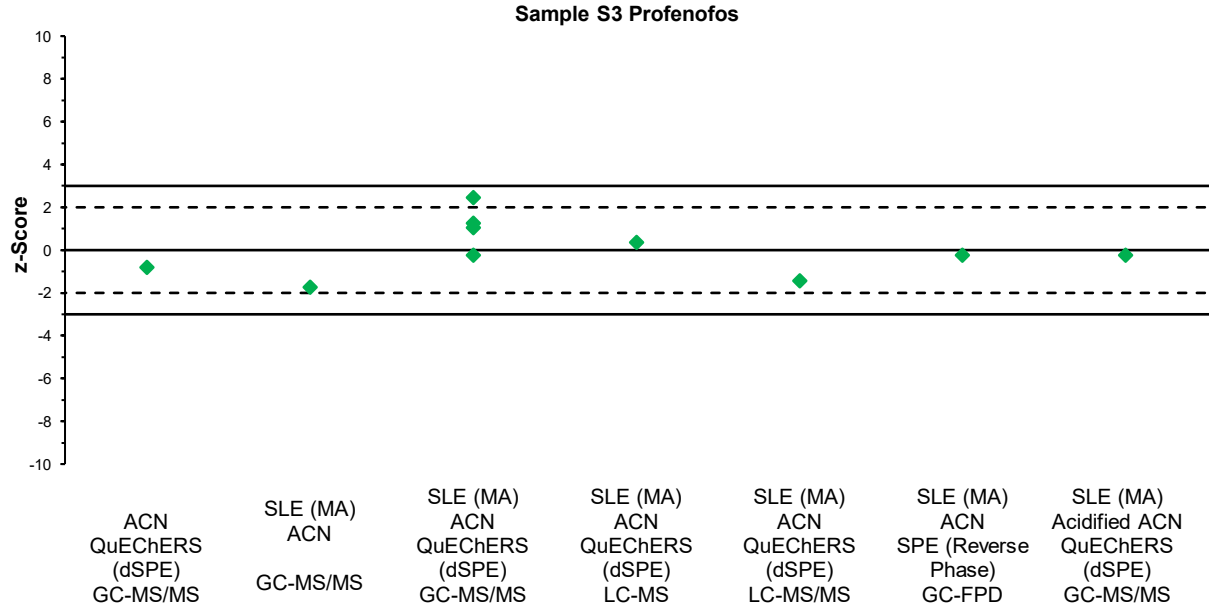


Figure 55 Sample S3 Profenofos *z*-Scores vs Methodology

Thiometon Participants were requested to report only for the named analyte, and not for breakdown products or metabolites. Four participants reported results for this analyte, and all results were significantly lower than the spiked value (Figure 56).

The low recovery is most likely due to the conversion of this analyte into thiometon sulfoxide and/or thiometon sulfone (which participants were not requested to report for) over the course of the PT study. Results from testing performed by NMIA Food & Health Chemical Laboratory are presented in Figure 57. Various conditions were assessed, including number of

freeze-thaw cycles and long-term stability. Higher thiometon was recovered when the sample underwent fewer freeze-thaw cycles, though in all cases there was significant conversion to thiometon sulfoxide. Results sheets will be updated in future to include common breakdown products and/or metabolites as separate analytes participants can report results for, to monitor for potential stability issues.

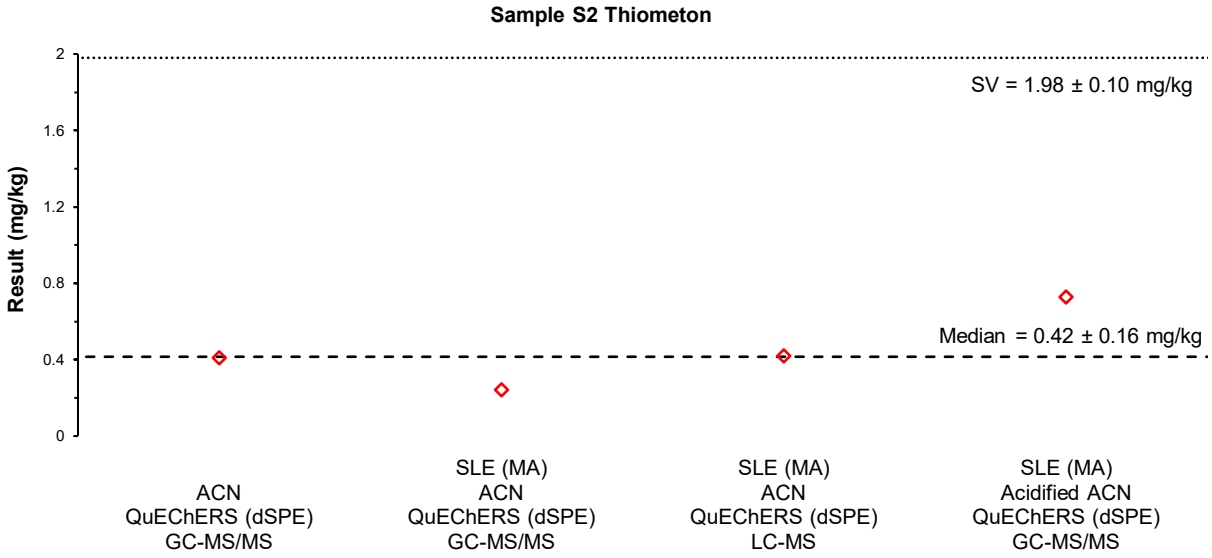


Figure 56 Sample S2 Thiometon Results vs Methodology

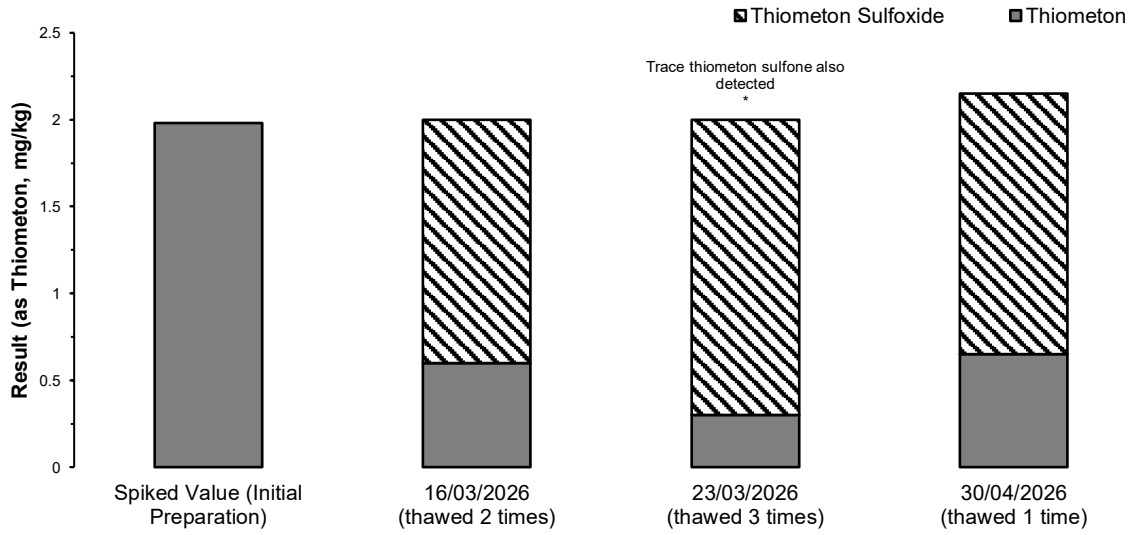


Figure 57 Sample S2 Thiometon Results vs Analysis Date and Number of Defrosts

Pilot Sample S4

Sample S4 maleic hydrazide in garlic was included as a pilot sample in this study in response to requests from participants.

Maleic hydrazide in garlic was first introduced in AQA 24-05 Sample S3, where it was spiked at 16.0 mg/kg. Only three participants reported numeric results, ranging from 1.73 mg/kg to 3.99 mg/kg. This analyte is prone to degradation when in contact with cut garlic, which was the likely reason for the low recovery of maleic hydrazide by participants.

For the present study, precautions were taken to ensure that the garlic puree was kept cold during the entire sample preparation procedure, to suppress enzymatic activity and reduce oxidation-related losses of maleic hydrazide. Participants were also instructed to minimise the total time that the sample was not frozen, and to avoid multiple freeze-thaw cycles. The analyte was spiked at 12.9 mg/kg. Four participants reported numeric results, and the results ranged from 0.72 mg/kg to 4.2 mg/kg (Figure 58).

The form of the maleic hydrazide may be one of the causes for the variability of the reported results. In this study, the garlic was spiked with a maleic hydrazide standard, whereas commercial formulations may instead contain maleic hydrazide potassium salt. This may be affecting the absorption of the analyte into the matrix. Further investigation will be conducted in the next PT study.

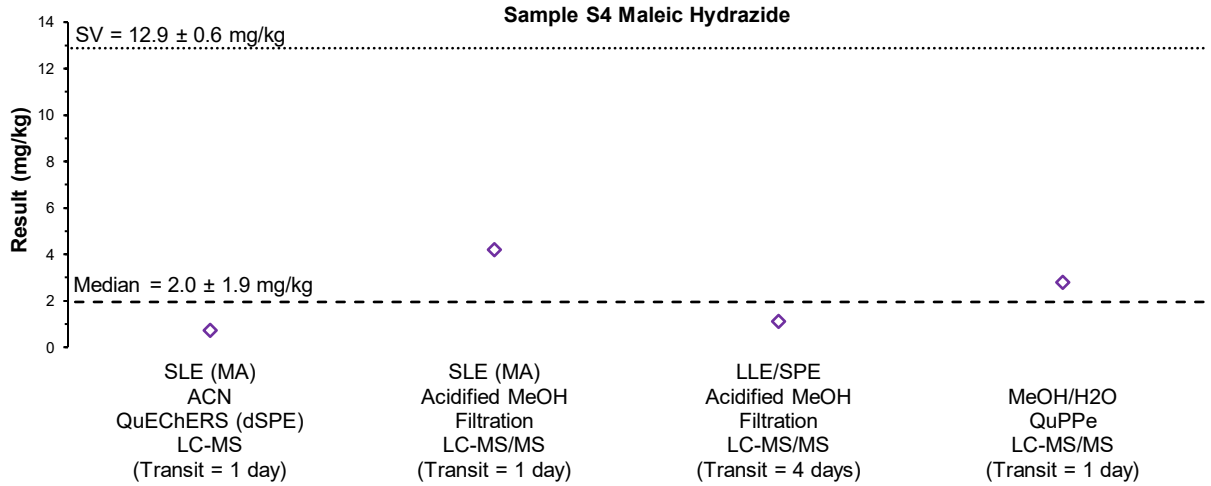


Figure 58 Sample S4 Maleic Hydrazide Results vs Methodology

6.10 Certified Reference Materials

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

- AccuStandard
- CPAChem
- Sigma-Aldrich
- ISO 17034 accredited standards
- Other certified standards and compounds

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'*[13]

6.11 Effect of Sample Matrix

A summary of the results reported, and acceptable *z*-scores obtained for each scored matrix, is presented in Table 40.

Participants tested for (and reported numeric results) for a similar proportion of analytes across all of Samples S1, S2, and S3.

Participants performed the best in Sample S3 hemp flour, with 92% of scored results returning acceptable *z*-scores.

Table 40 Performance by Matrix

Sample	Expected Number of Results	Numeric Results Reported (% of expected number of results)	*z*-Scores Calculated (% of numeric results reported)	Acceptable *z*-Scores (% of *z*-Scores Calculated)
S1 Tomato	128	91 (71%)	85 (93%)	75 (88%)
S2 Blueberry	135	97 (72%)	73 (75%)	62 (85%)
S3 Hemp Flour	108	77 (71%)	62 (81%)	57 (92%)

6.12 Fitness for Purpose of Pesticide Results

One standard that sets MRLs to food products in Australia is the FSANZ Food Standards Code.[5] Laboratories need to ensure accurate measurements of these food products, so that their result correctly reflects whether a sample is compliant with the relevant MRL. The MRLs for analytes in this study are presented in Table 1.

When a test result is used to determine whether a sample complies with an upper control limit, the measurement uncertainty of that result is critical. ISO/IEC 17025 defines a decision rule for such assessments as a 'rule that describes how measurement uncertainty is accounted for when stating conformity with a specified requirement'.[9] To determine whether a sample meets a regulatory limit, considering the reported result and its associated uncertainty, decision rules generally provide three possible outcomes: Pass, Fail, or Inconclusive when further testing may be required (Figure 59).[14]

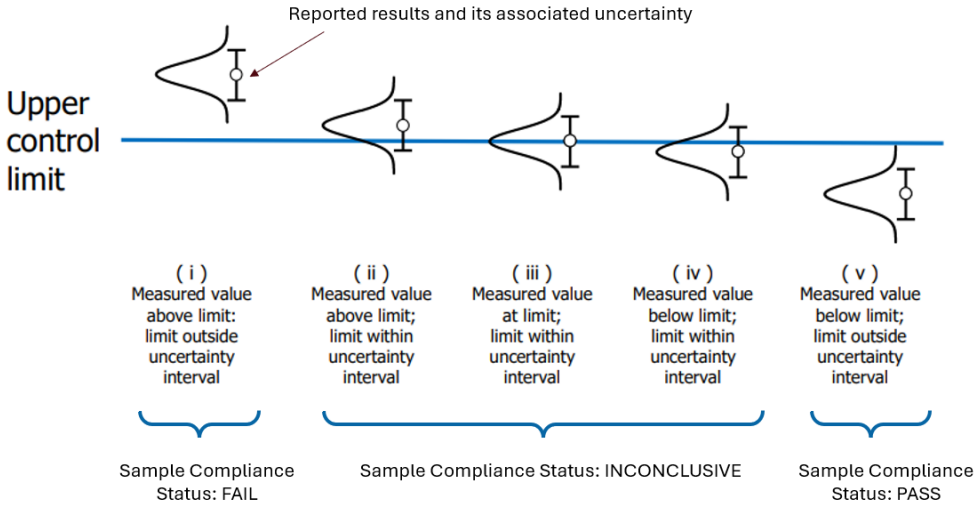


Image adapted from: Eurachem/CITAC Guide Use of Uncertainty Information in Compliance Assessment[14]

Figure 59 Assessment of Compliance with an Upper Limit

Figures 60 to 76 show comparisons of the spiked value (SV), assigned value (AV), participants' results, and MRLs for scored analytes. In some cases, the MRL refers to the sum of a number of different permitted residues,[5] and not only the named analyte given here. For

this study, all AVs were in agreement with SVs with respect to being above (non-compliant) or below (compliant) the relevant MRL.

The majority of participants' results correctly reflected compliance or non-compliance, uncertainty considered. Analytes which challenged participants are discussed below.

S1 Tomato Buprofezin The assigned value (0.76 ± 0.11 mg/kg) reflected that this sample was compliant with the MRL (1 mg/kg). While all participants reported correctly results below the MRL, Laboratories 2, 3, 6, and 9 returned inconclusive compliance statuses as their uncertainties spanned the MRL.

Due to the assigned value being close to the MRL, a participant using a routine method and reporting an acceptable result with a reasonable uncertainty evaluation, may be expected to return an inconclusive compliance status, particularly if the laboratory is slightly biased high. However, laboratories are advised to investigate and correct for bias, as an inconclusive compliance status based on their results may lead to unnecessary additional analyses.

S1 Tomato Indoxacarb Sample S1 was not compliant for indoxacarb as the assigned value (0.256 ± 0.043 mg/kg) was above the MRL of 0.2 mg/kg.

Most participants correctly reported results that reflected samples' non-compliance status, however, Laboratories 3, 6, 12, 14, and 17 reported uncertainties spanning or at the MRL, deeming compliance status of the sample as inconclusive.

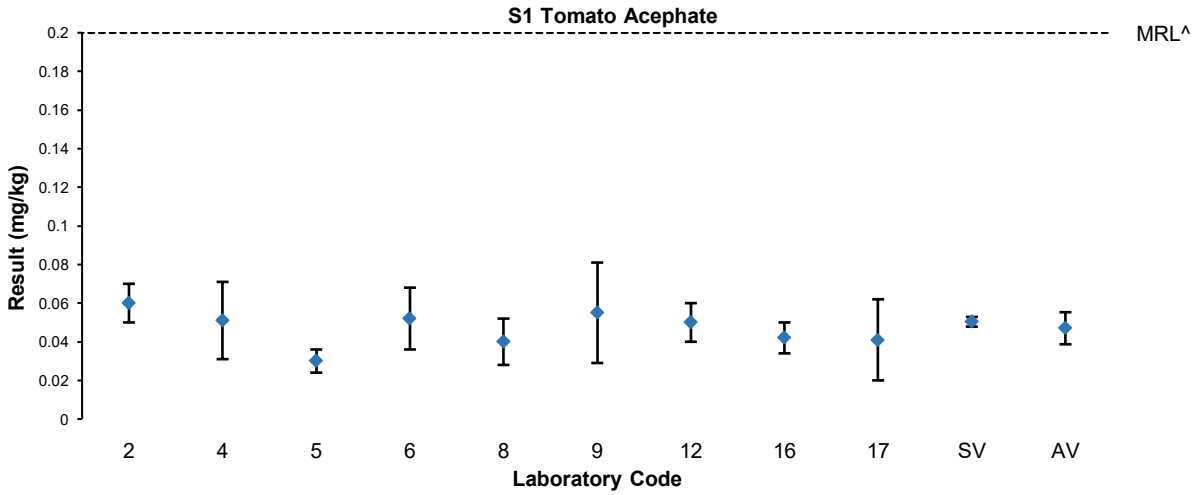
Due to the assigned value being close to the MRL, a participant using a routine method and reporting an acceptable result with a reasonable uncertainty evaluation, may be expected to return an inconclusive compliance status, particularly if the laboratory is slightly biased low.

Additionally, Laboratories 1, 8 and 11 incorrectly reported results below the MRL, though with uncertainties spanning the MRL (inconclusive compliance status).

S2 Blueberry Chlorpyrifos The assigned value (0.0292 ± 0.0047 mg/kg) was almost three times higher than the MRL (0.01 mg/kg).

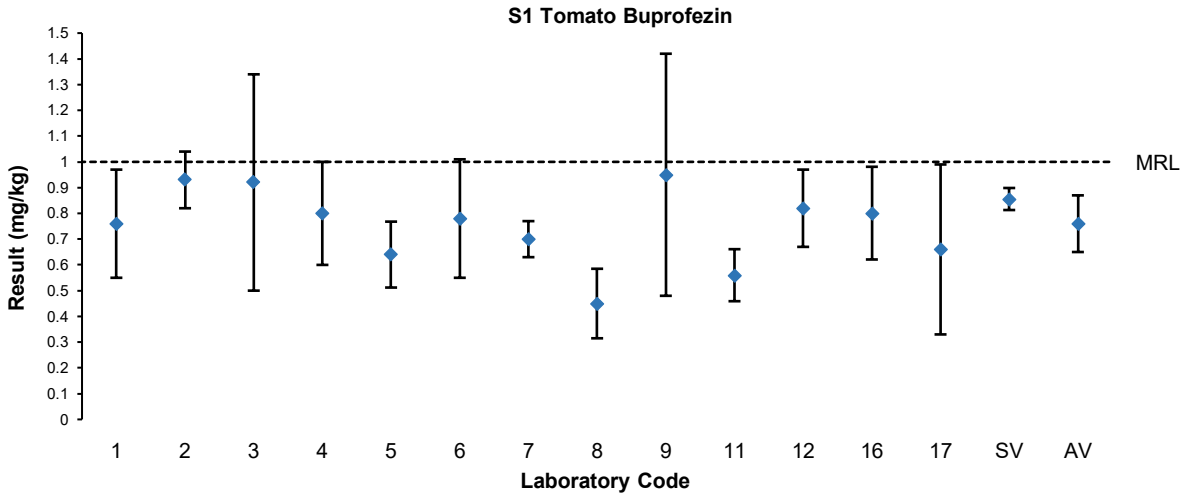
All participants correctly reported results indicating the sample's non-compliance status.

The uncertainty reported by Laboratory 7 spanned the MRL, leading to an inconclusive compliance status; this was due to the uncertainty being too large to be fit-for-purpose (100% relative of the reported result).



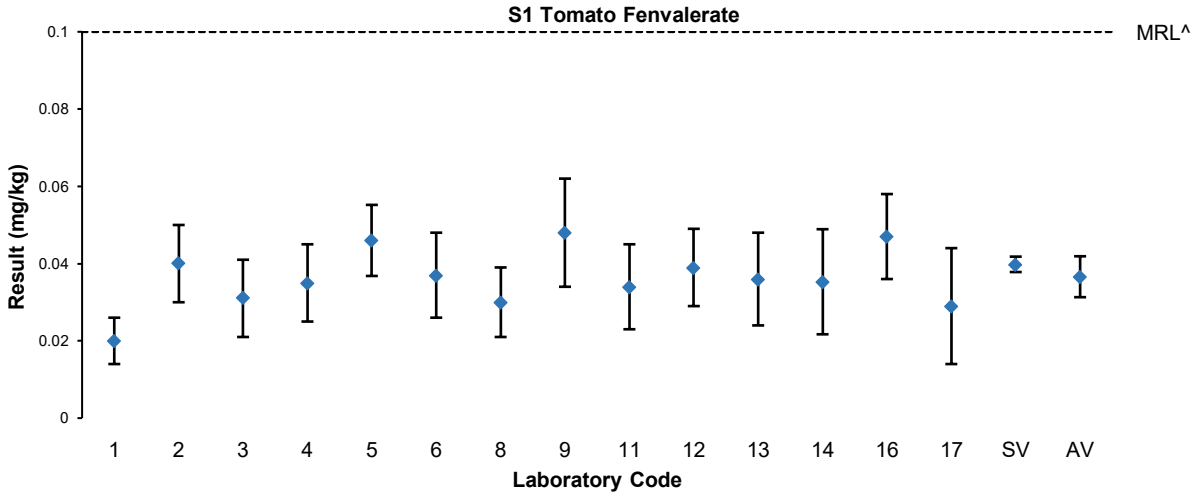
^MRL has been scaled to fit the chart; original value is 5 mg/kg
SV=Spike Value, AV=Assigned Value

Figure 60 Sample S1 Tomato Acephate Results and MRL



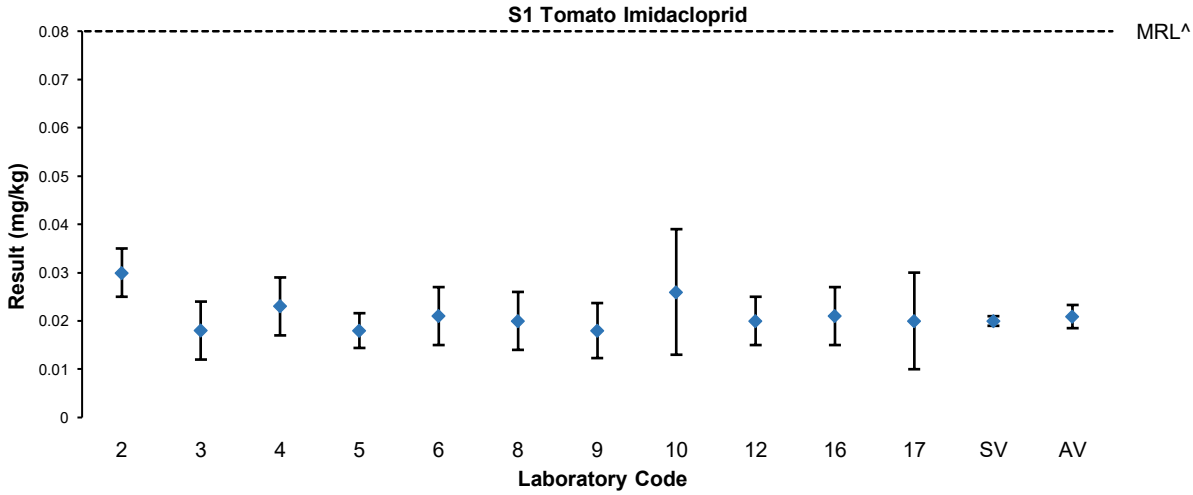
SV=Spike Value, AV=Assigned Value

Figure 61 Sample S1 Tomato Buprofezin Results and MRL



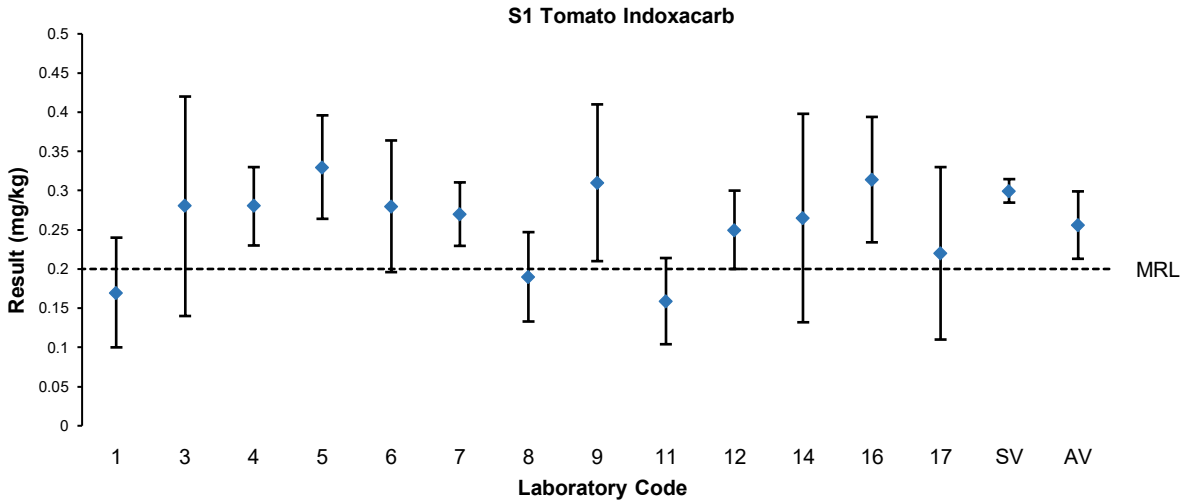
^MRL has been scaled to fit the chart; original value is 0.2 mg/kg
SV=Spike Value, AV=Assigned Value

Figure 62 Sample S1 Tomato Fenvalerate Results and MRL



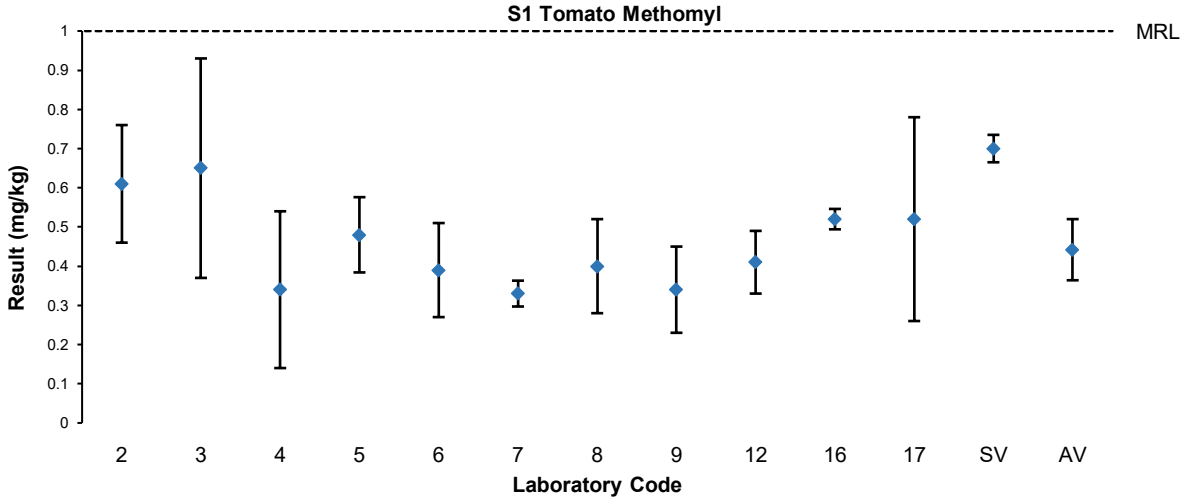
^MRL has been scaled to fit the chart; original value is 0.5 mg/kg
SV=Spike Value, AV=Assigned Value

Figure 63 Sample S1 Tomato Imidacloprid Results and MRL



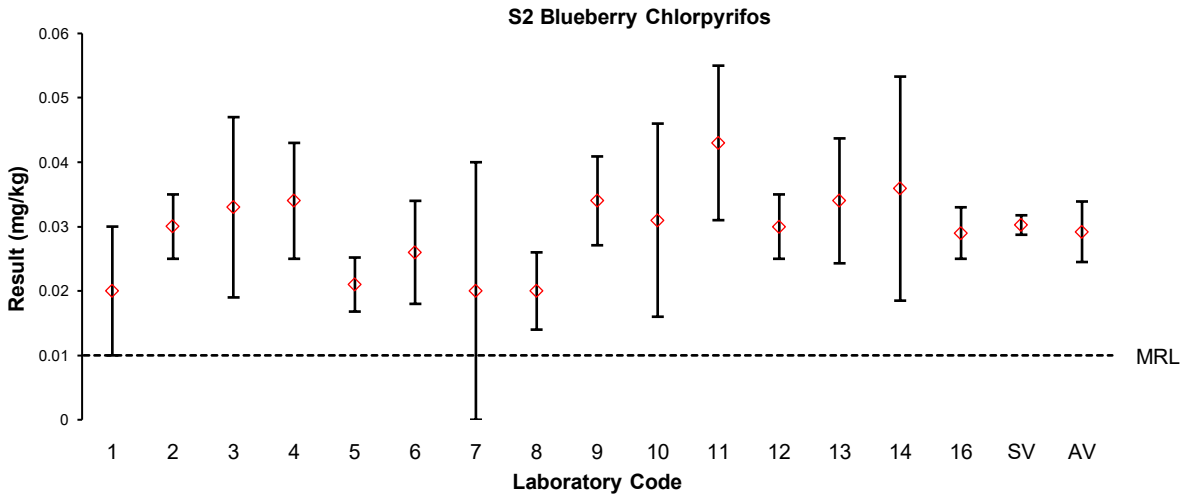
SV=Spike Value, AV=Assigned Value

Figure 64 Sample S1 Tomato Indoxacarb Results and MRL



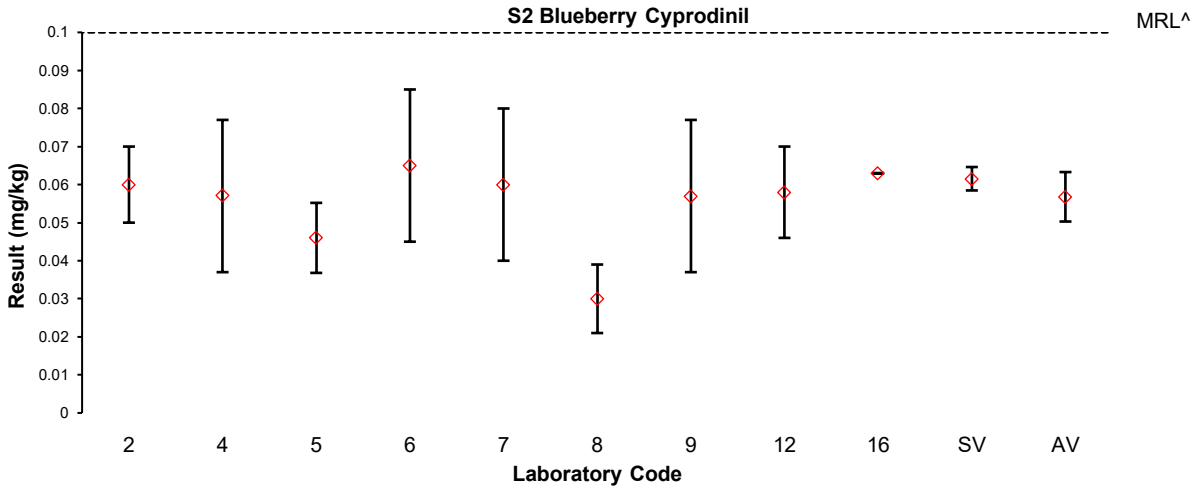
SV=Spike Value, AV=Assigned Value

Figure 65 Sample S1 Tomato Methomyl Results and MRL



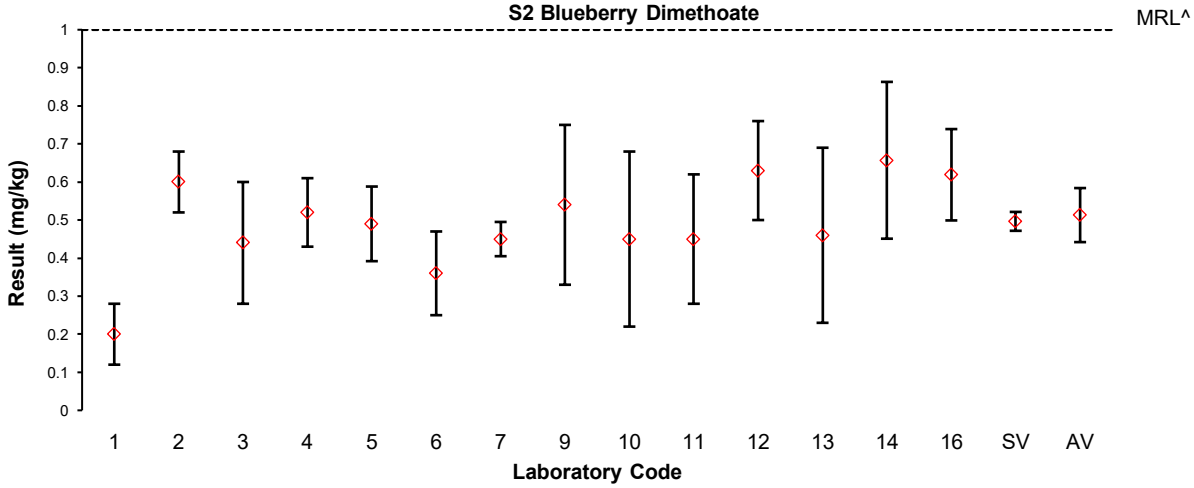
SV=Spike Value, AV=Assigned Value

Figure 66 Sample S2 Blueberry Chlorpyrifos Results and MRL



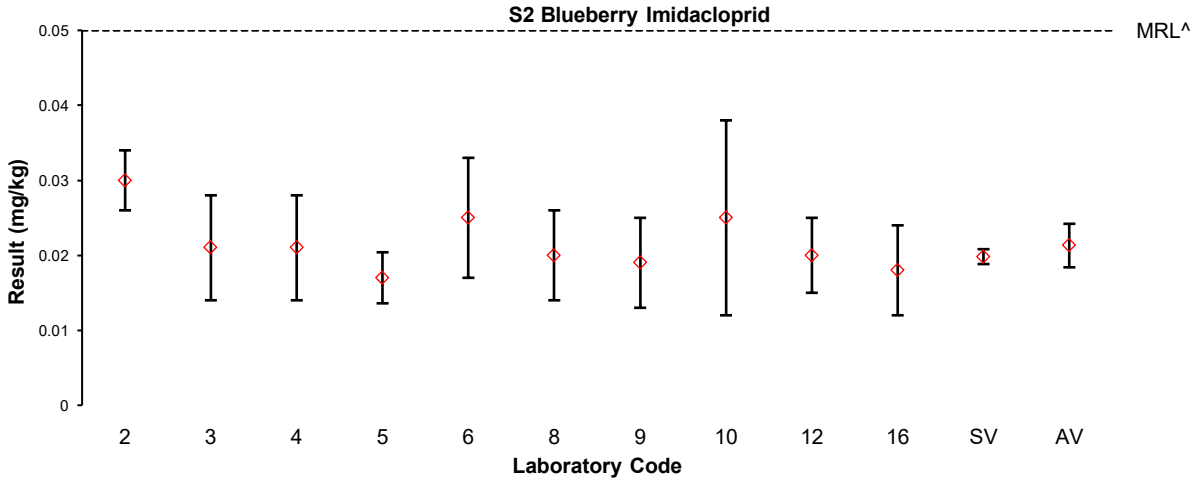
^MRL has been scaled to fit the chart; original value is 3 mg/kg
SV=Spike Value, AV=Assigned Value

Figure 67 Sample S2 Blueberry Cyprodinil Results and MRL



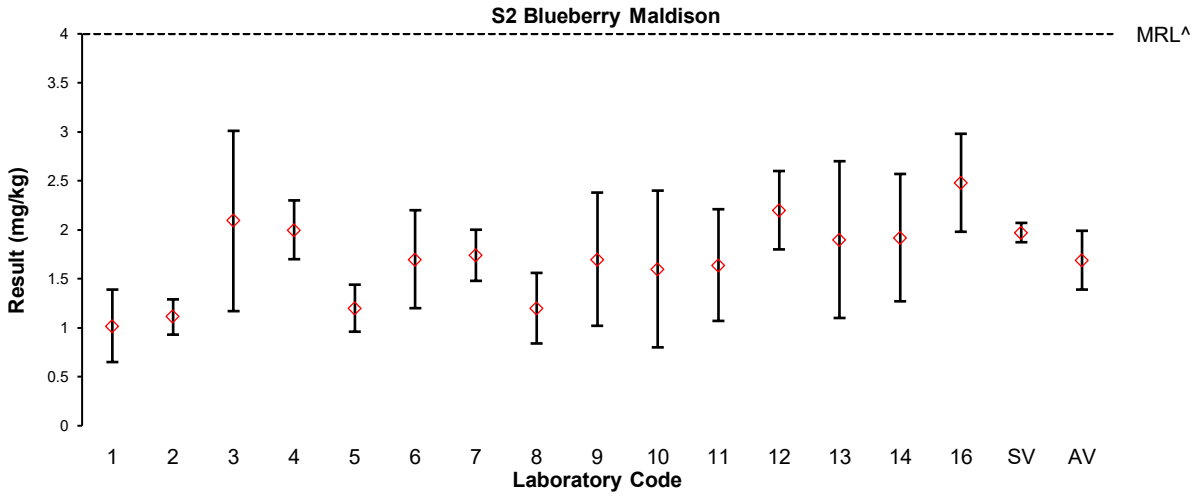
^MRL has been scaled to fit the chart; original value is 5 mg/kg.
SV=Spike Value, AV=Assigned Value

Figure 68 Sample S2 Blueberry Dimethoate Results and MRL



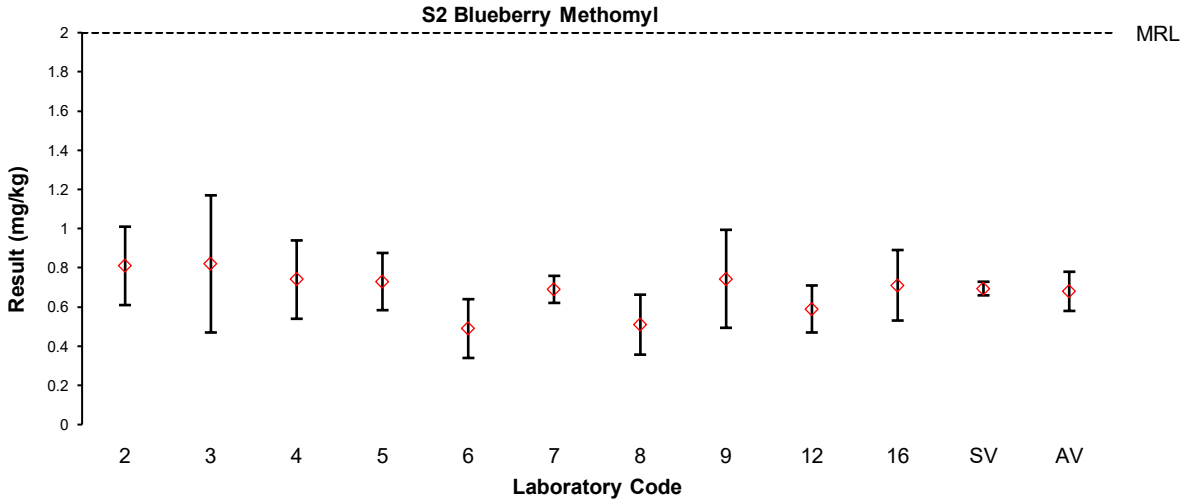
^MRL has been scaled to fit the chart; original value is 3.5 mg/kg.
SV=Spike Value, AV=Assigned Value

Figure 69 Sample S2 Blueberry Imidacloprid Results and MRL



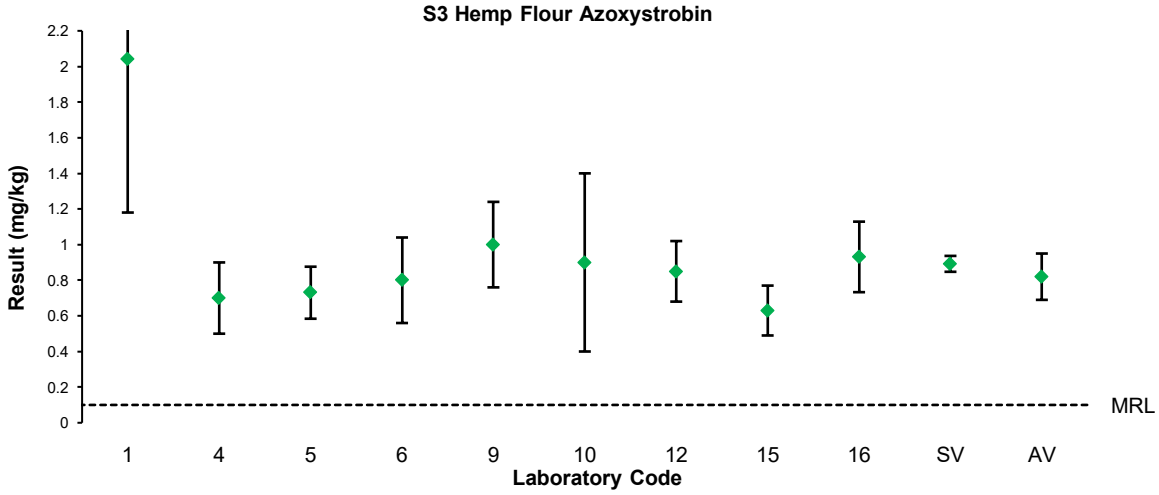
^MRL has been scaled to fit the chart; original value is 10 mg/kg.
SV=Spike Value, AV=Assigned Value

Figure 70 Sample S2 Blueberry Maldison Results and MRL



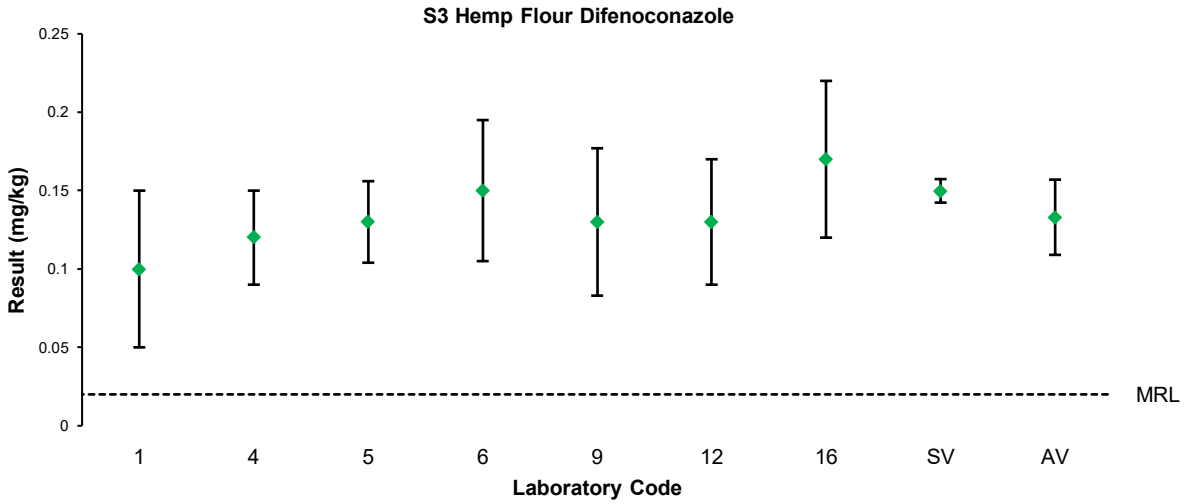
SV=Spike Value, AV=Assigned Value

Figure 71 Sample S2 Blueberry Methomyl Results and MRL



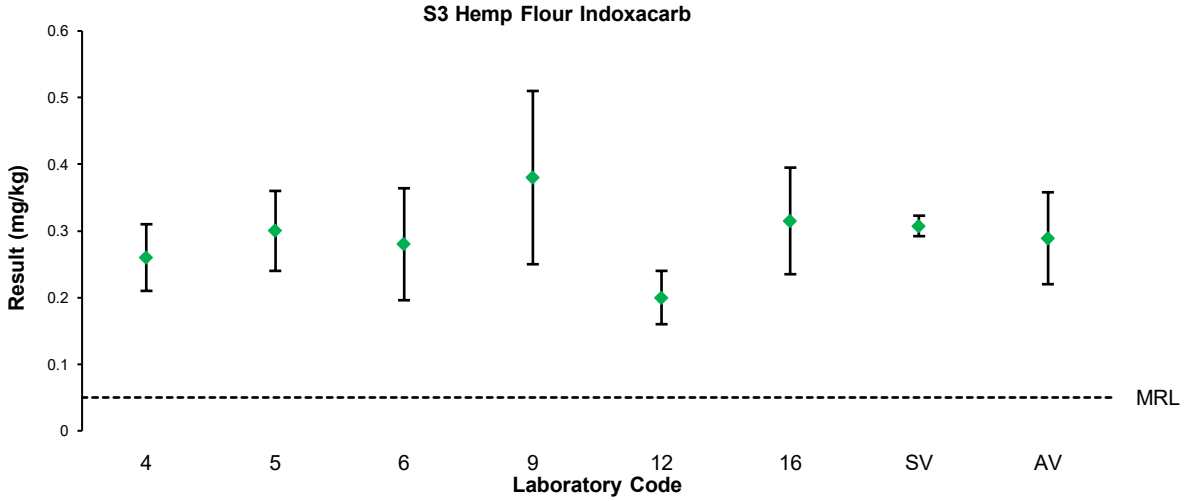
SV=Spike Value, AV=Assigned Value

Figure 72 Sample S3 Hemp Flour Azoxystrobin Results and MRL



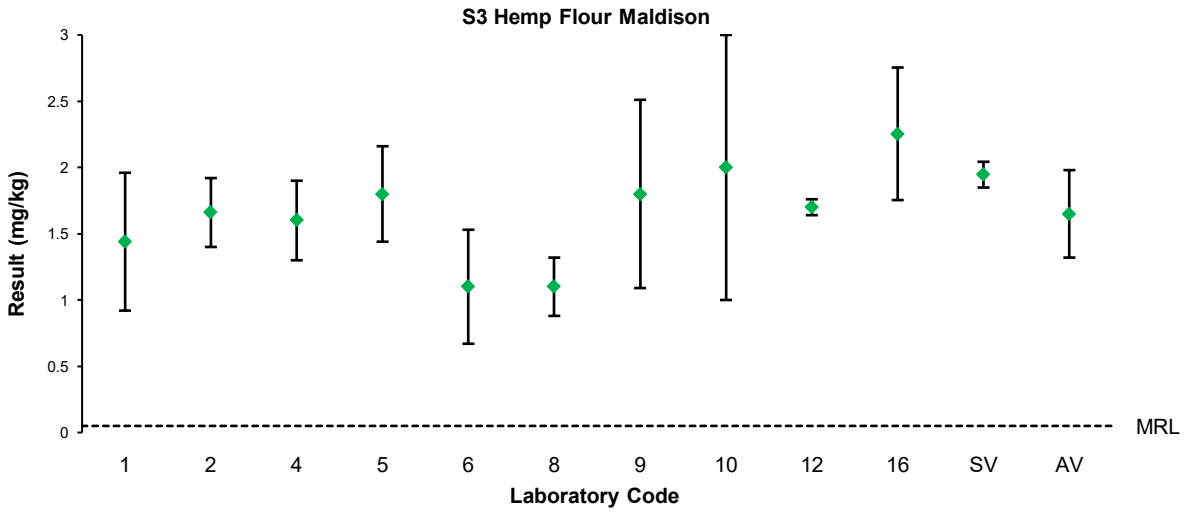
SV=Spike Value, AV=Assigned Value

Figure 73 Sample S3 Hemp Flour Difenoconazole Results and MRL



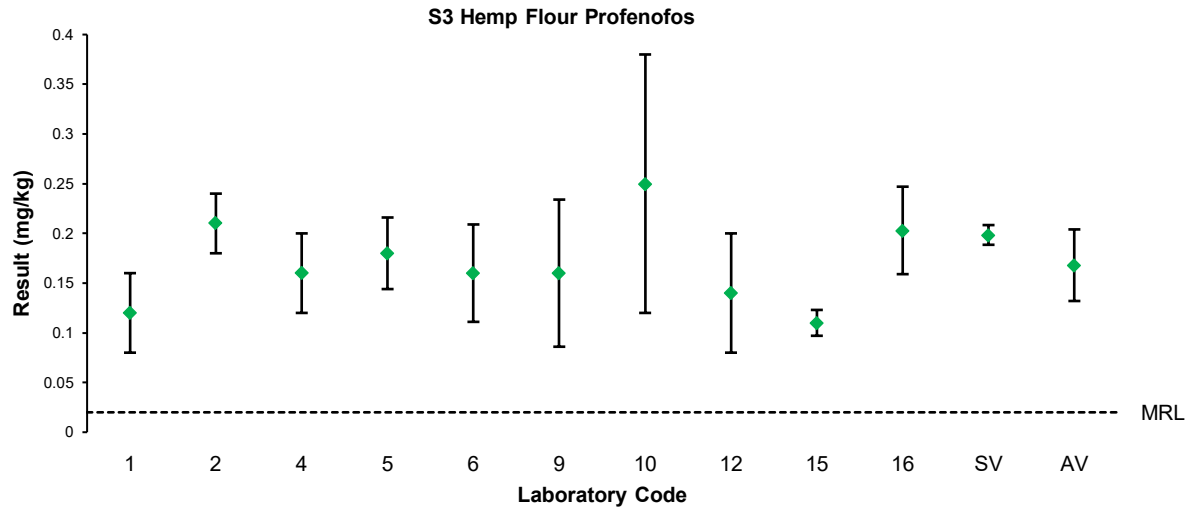
SV=Spike Value, AV=Assigned Value

Figure 74 Sample S3 Hemp Flour Indoxacarb Results and MRL



SV=Spike Value, AV=Assigned Value

Figure 75 Sample S3 Hemp Flour Maldison Results and MRL

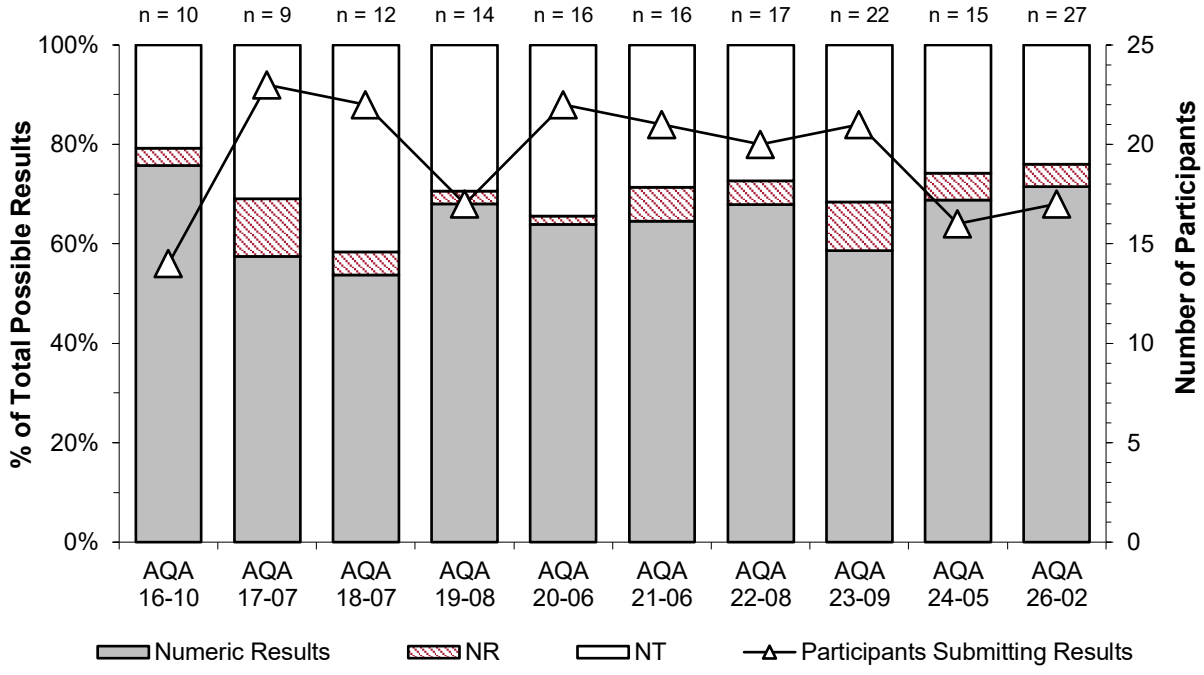


SV=Spike Value, AV=Assigned Value

Figure 76 Sample S3 Hemp Flour Profenofos Results and MRL

6.13 Comparison with Previous Pesticides in Food PT Studies

A summary of participation and reported results rates in NMIA Pesticides in Food PT studies over the last 10 studies (2016 to 2026) is presented in Figure 77. The numeric results reported by participants have remained steady over this period.



n = number of included analytes

Figure 77 Summary of Participation and Reported Results in NMIA Pesticides in Food PT Studies

A summary of the acceptable performance (presented as a percentage of the total number of scores for each study) in NMIA Pesticides in Food PT studies over the last 10 studies (2016 to 2026) is presented in Figure 78. This study represents the best performance by participants over this period. The proportion of acceptable z-scores and E_n-scores over this period has on average been 78% and 73% respectively.

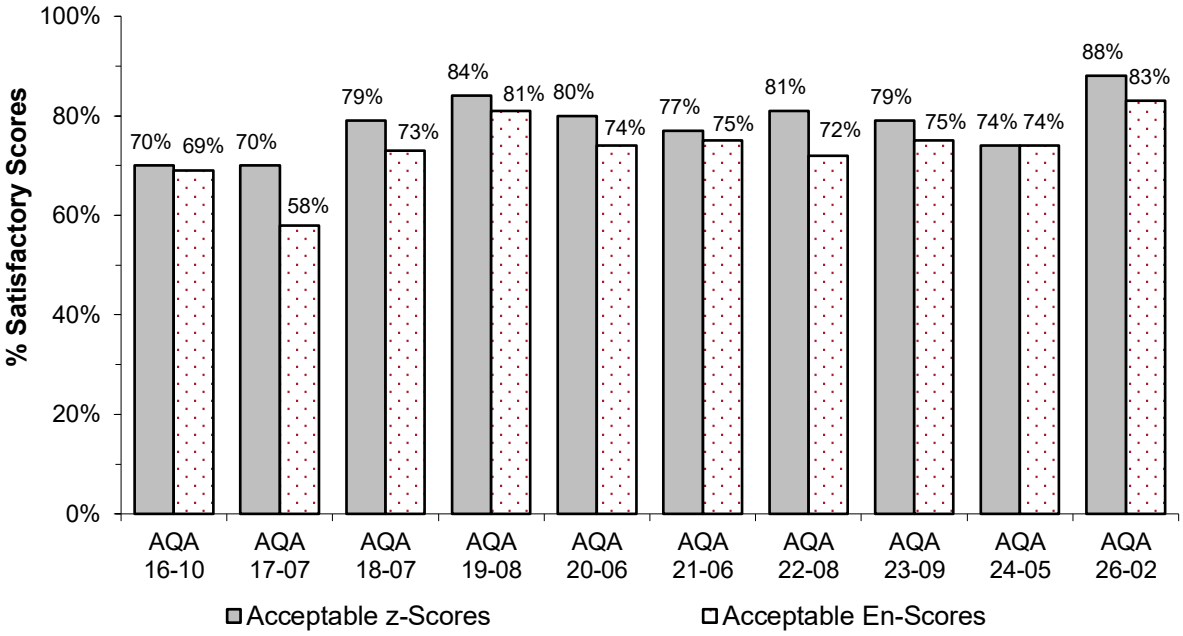


Figure 78 Summary of Participants' Performance in NMIA Pesticides in Food PT Studies

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

As discussed in Section 6.2, it is a requirement of ISO/IEC 17025 that laboratories report their uncertainties.[9] Figure 79 presents a summary of the relative uncertainties as reported by participants over the last 10 studies (2016 to 2026). Over this time period, most numeric results were reported with uncertainties (average of 89% per study). An average of 67% of participants in each study reported that they were accredited to ISO/IEC 17025.

Most participants over this time period reported realistic and fit-for-purpose relative expanded uncertainties between 15% and 50%, and the proportion of these relative uncertainties have been increasing (improving) over the last few studies.

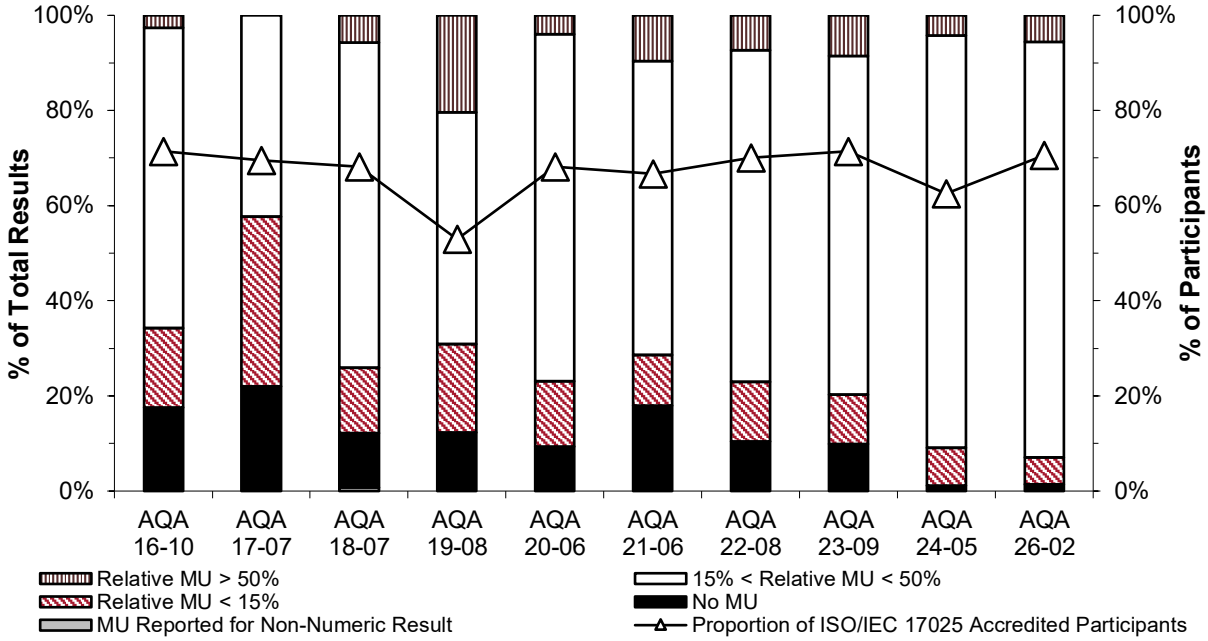


Figure 79 Summary of Participant' Relative Uncertainties for NMIA Pesticides in Food PT Studies

7 REFERENCES

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

[1] ISO/IEC 17043, *Conformity assessment – General requirements for the competence of proficiency testing providers.*

[2] Commonwealth of Australia, Department of Industry, Science and Resources, NMIA, 2026, *Study Protocol for Proficiency Testing,* viewed May 2026, <https://www.industry.gov.au/sites/default/files/2020-10/cpt_study_protocol.pdf>.

[3] Commonwealth of Australia, Department of Industry, Science and Resources, NMIA, 2026, *Chemical Proficiency Testing Statistical Manual*, viewed May 2026, <https://www.industry.gov.au/sites/default/files/2019-07/cpt_statistical_manual.pdf>.

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

[5] Federal Register of Legislation, 2026, *Australia New Zealand Food Standards Code – Schedule 20 – Maximum residue limits,* viewed May 2026*,* <https://www.legislation.gov.au/F2015L00468/latest/text>.

[6] Food and Agriculture Organization of the United Nations, *NSP - List of Pesticides evaluated by JMPS and JMPR*, viewed May 2026, <https://www.fao.org/agriculture/crops/thematic-sitemap/theme/pests/lpe/en/>.

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

[8] Thompson, M., 2000, 'Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing', *Analyst*, vol. 125, pp. 385-386.

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

[10] Eurachem/CITAC Guide CG 4, QUAM:2012.P1, *Quantifying Uncertainty in Analytical Measurement*, 3rd edition, viewed May 2026, <http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf>.

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

[12] Anastassiades, M., Schäfer A.-K., Eichhorn, E., Kolberg, D. I., Dias, H., Benkenstein, A., Zechmann, S., Mack, D., Wildgrube, C, Barth, A., Sauer, B., Sigalov, I., Goerlich, S., Dörk, D., and Cerchia, G., 2024, 'Quick Method for the Analysis of Highly Polar Pesticides in Food Involving Extraction with Acidified Methanol and LC- or IC-MS/MS Measurement I. Food of Plant Origin (QuPPe-PO-Method)', version 12.3, viewed May 2026, <https://www.eurl-pesticides.eu/userfiles/file/EurlSRM/EurlSrm_meth_QuPPe_PO_V12_3.pdf>

[13] BIPM, JCGM 200:2012, *International vocabulary of metrology – Basic and general concepts and associated terms (VIM)*, 3rd edition, viewed May 2026, <https://www.bipm.org/utils/common/documents/jcgm/JCGM_200_2012.pdf>.

[14] Eurachem/CITAC Guide *Use of Uncertainty Information in Compliance Assessment,* 2nd ed., viewed May 2026, <https://www.eurachem.org/images/stories/Guides/pdf/MUC2021_P1_EN.pdf>

[15] Federal Register of Legislation, 2026, *Australia New Zealand Food Standards Code – Schedule 22 – Foods and classes of foods*, viewed May 2026, <https://www.legislation.gov.au/F2015L00433/latest/text>.

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

APPENDIX 1 SAMPLE PREPARATION

Tomatoes were bought from a local organic fruit and vegetable wholesaler. Blueberries and garlic were bought from local grocery stores. Hemp flour was bought from an online retailer. The portion of fruit and vegetables prepared was in accordance with the Australian New Zealand Food Standards Code – Schedule 22 – Foods and classes of foods.[15]

Preparation of Sample S1 (Tomato)

The tomatoes were rinsed using tap water and allowed to air dry. The tomatoes were pureed and passed through an 850 µm sieve. Aliquots of at least 100 g were dispensed to provide unspiked samples. The remaining puree was spiked with pesticide standard solutions and stirred, before aliquots of at least 100 g were dispensed to provide spiked samples. Each bottle was then labelled, shrink-wrapped and placed in a freezer.

Preparation of Sample S2 (Blueberries)

The blueberries were rinsed with tap water and allowed to air dry. The blueberries were pureed and passed through an 850 µm sieve. Aliquots of at least 100 g were dispensed to provide unspiked samples. The remaining puree was spiked with pesticide standard solutions and stirred, before aliquots of at least 100 g were dispensed to provide spiked samples. Each bottle was then labelled, shrink-wrapped and placed in a freezer.

Preparation of Sample S3 (Hemp Flour)

Aliquots of at least 20 g hemp flour were dispensed to provide unspiked samples. Hemp flour was then suspended in acetone, spiked with pesticide standard solutions, and stirred, allowing the acetone to evaporate off. Aliquots of at least 20 g were then dispensed to provide spiked samples. Each bottle was then labelled, vacuum-sealed, and placed in a freezer.

Preparation of Sample S4 (Garlic)

Garlic cloves were pureed and passed through an 850 µm sieve. The puree was kept chilled throughout the whole sample preparation procedure. Aliquots of at least 20 g were dispensed to provide unspiked samples. The remaining puree was then spiked with a maleic hydrazide standard solution and mixed, before aliquots of at least 20 g were dispensed to provide spiked samples. Each bottle was then labelled, put into a press-seal bag, wrapped with gel-ice, and placed in a freezer.

APPENDIX 2 HOMOGENEITY AND STABILITY ASSESSMENT

A2.1 Homogeneity

The samples were prepared using a process previously demonstrated to produce sufficiently homogeneous samples for similar analytes and matrices as Samples S1, S2, and S4.

Homogeneity testing was conducted for Sample S3 as this was a new type of matrix.

Sample S3 Homogeneity Testing

Homogeneity testing was conducted for Sample S3 azoxystrobin, cypermethrin, and diazinon. The testing was performed using routine methods from the NMIA Analytical Services Branch.

For azoxystrobin: Sample (1 g) was weighed out, and extraction solvent (2% formic acid in ACN, 10 mL) was added. Samples were tumbled for 10 minutes, followed by centrifuging for at 4000 rpm for 5 minutes. Sample extract (1 mL) was diluted with more extraction solvent (1 mL) and vortexed to form a diluted extract. The diluted extract (1 mL) was added to a QuEChERS filter, where it was vortexed for 30 seconds, followed by centrifuging at 3500 rpm for 5 minutes. The filtered extract (200 µL) was then transferred into a 0.2 µm 2 mL filter tube, followed by deionized water (200 µL). Surrogate/internal standard (25 µL) was added to the filter tube before it was centrifuged at 2500 rpm for 5 minutes. The filtered mixture was then analysed by LC-MS/MS.

For cypermethrin and diazinon: Sample (1 g) was weighed out, and extraction solvent (2% formic acid ACN, 20 mL) was added. Samples were tumbled for 10 minutes, followed by centrifuging at 4000 rpm for 5 minutes. Sample extract (1.5 mL) was passed through an Agilent C18 Endcapped SPE into a QuEChERS filter. The QuEChERS filter was capped and vortexed for 30 seconds followed by centrifuging at 3500 rpm for 5 minutes. Internal standard (5 µL) was added to the filtered extract (200 µL), and this was analysed by GC-MS/MS.

Homogeneity testing for this sample was based on that described by Thompson and Fearn,[16] which is also the procedure described in the International Harmonized Protocol for Proficiency Testing.[4] A minimum of six containers from Sample S3 were selected at random. Duplicate test portions were taken from each container, and the concentration of the targeted analytes were measured. Measurements were made under repeatability conditions in random order. The data for the full homogeneity testing of Sample S3 can be found below in Tables 41 to 43.

Samples were found to be sufficiently homogeneous for use in a PT study with a SDPA (as PCV) of 20%.

Table 41 Homogeneity Testing for Sample S3 Azoxystrobin

Bottle Number	S3 Azoxystrobin (mg/kg)	
	Replicate 1	Replicate 2
1	0.58	0.57
11	0.60	0.55
12	0.62	0.57
26	0.56	0.61
33	0.56	0.62
44	0.61	0.59
48	0.60	0.57
Average	0.59	
CV	3.9%	

Thompson and Fearn Homogeneity Tests[16]

Test	Value	Critical	Result
Cochran	0.30	0.73	**Pass**
s_{an}/σ	0.25	0.50	**Pass**
s^2_{sam}	0.00001	0.0038	**Pass**

Table 42 Homogeneity Testing for Sample S3 Cypermethrin

Bottle Number	S3 Cypermethrin (mg/kg)	
	Replicate 1	Replicate 2
1	1.19	1.17
11	1.22	1.15
12	1.11	1.15
33	1.06	1.05
44	1.27	1.19
48	1.20	1.20
Average	1.16	
CV	5.6%	

Thompson and Fearn Homogeneity Tests[16]

Test	Value	Critical	Result
Cochran	0.47	0.78	**Pass**
s_{an}/σ	0.15	0.50	**Pass**
s^2_{sam}	0.0033	0.013	**Pass**

Table 43 Homogeneity Testing for Sample S3 Diazinon

Bottle Number	S3 Diazinon (mg/kg)	
	Replicate 1	Replicate 2
1	0.557	0.546
11	0.559	0.552
12	0.480	0.512
26	0.637	0.534
33	0.500	0.497
44	0.591	0.561
48	0.554	0.619
Average	0.550	
CV	8.2%	

Thompson and Fearn Homogeneity Tests[16]

Test	Value	Critical	Result
Cochran	0.62	0.73	**Pass**
s_{an}/σ	0.32	0.50	**Pass**
s^2_{sam}	0.00087	0.0040	**Pass**

A2.2 Stability

The samples were prepared, stored and dispatched using a process previously demonstrated to produce sufficiently stable samples for similar analytes and matrices as Samples S1 and S2, over a similar time frame. After preparation and before dispatch, samples were stored in a freezer at approximately -20 °C. For dispatch, samples were packaged into insulated polystyrene foam boxes with cooler bricks. No stability testing was performed for pilot Sample S4.

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

Sample S3 Stability Testing

Stability testing was conducted for Sample S3 azoxystrobin, cypermethrin, and diazinon with the testing being performed using the same routine methods from NMIA Analytical Services Branch as described above.

Figures 80 to 82 present the initial and stability testing results for each analyte. Results were in agreement with each other and were within their respective uncertainties.

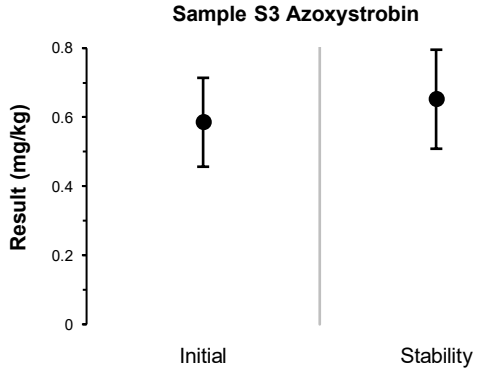


Figure 80 S3 Azoxystrobin Stability Results

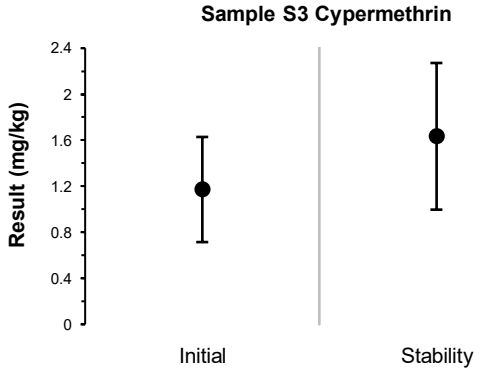


Figure 81 S3 Cypermethrin Stability Results

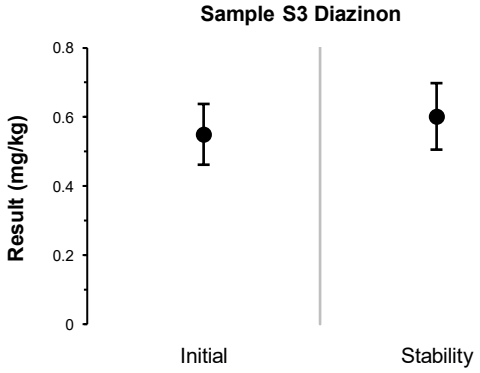


Figure 82 S3 Diazinon Stability Results

Comparison of Participants' Results and Sample Transit Time

Participants' results in this study also gave no reason to question the samples' transportation stability. Comparisons of results for all scored analytes to days spent in transit are presented in Figures 83 to 102 (blue solid lines are AV ± U).

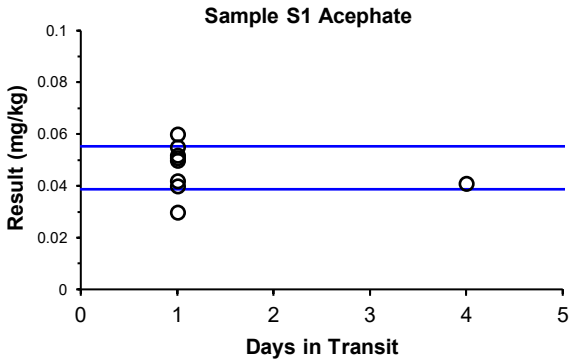


Figure 83 S1 Acephate Results vs Transit Days

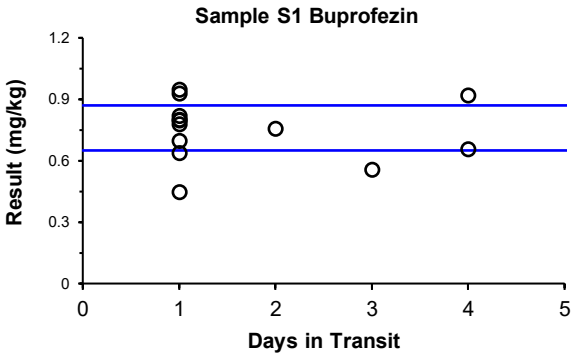


Figure 84 S1 Buprofezin Results vs Transit Days

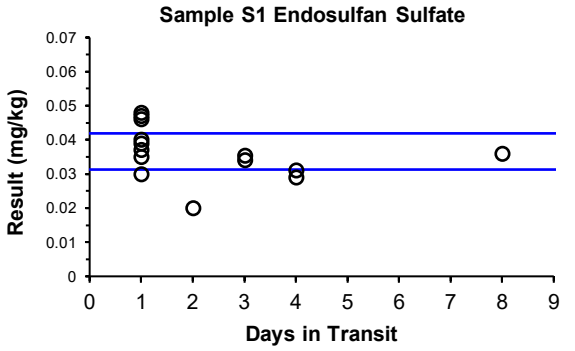


Figure 85 S1 Endosulfan Sulfate Results vs Transit Days

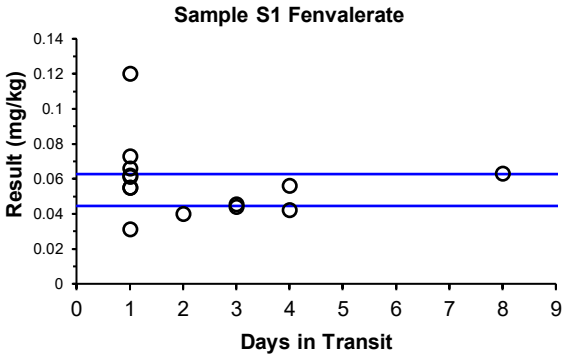


Figure 86 S1 Fenvalerate Results vs Transit Days

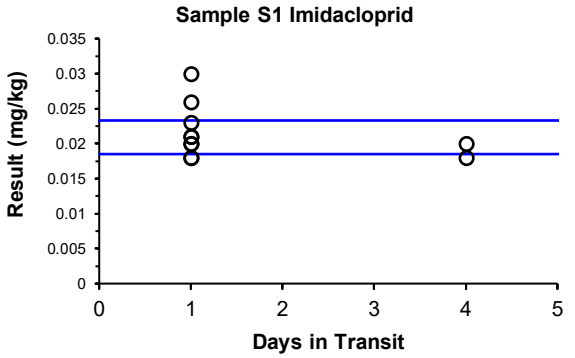


Figure 87 S1 Imidacloprid Results vs Transit Days

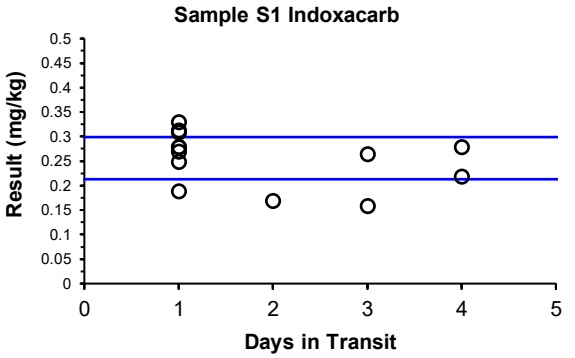


Figure 88 S1 Indoxacarb Results vs Transit Days

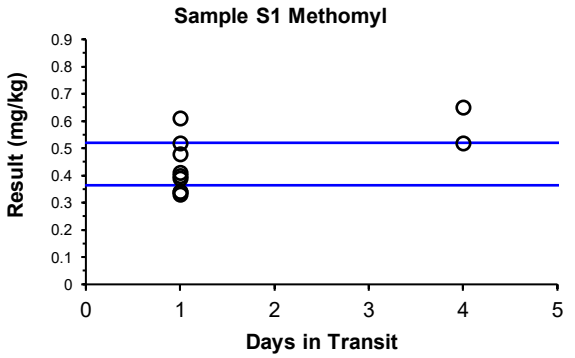


Figure 89 S1 Methomyl Results vs Transit Days

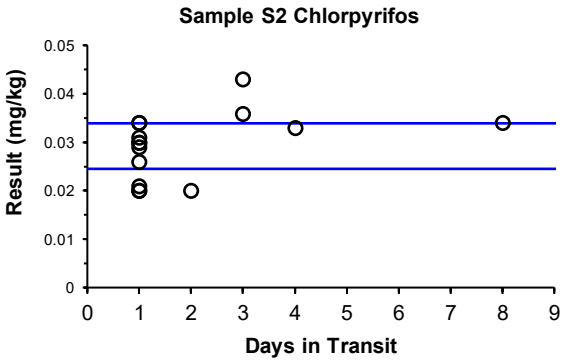


Figure 90 S2 Chlorpyrifos Results vs Transit Days

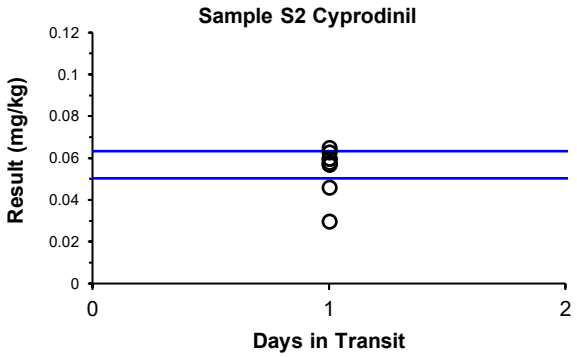


Figure 91 S2 Cyprodinil Results vs Transit Days

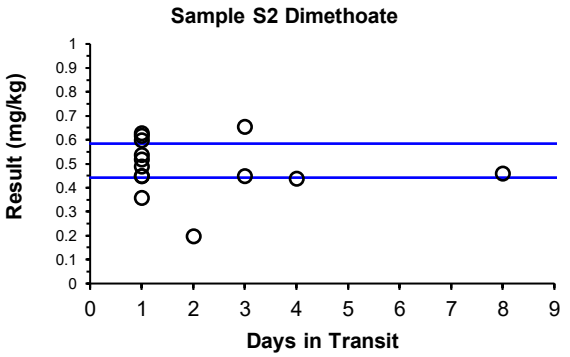


Figure 92 S2 Dimethoate Results vs Transit Days

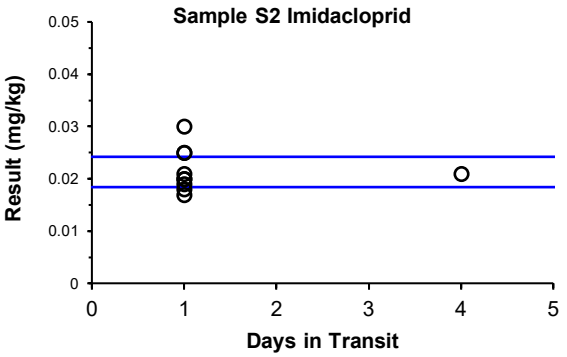


Figure 93 S2 Imidacloprid Results vs Transit Days

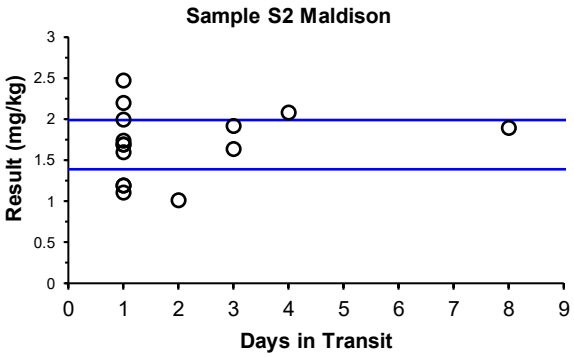


Figure 94 S3 Maldison Results vs Transit Days

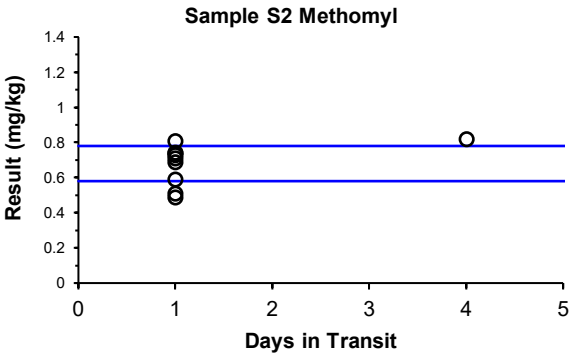


Figure 95 S2 Methomyl Results vs Transit Days

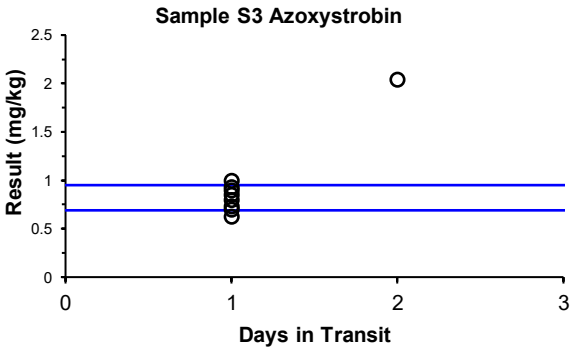


Figure 96 S3 Azoxystrobin Results vs Transit Days

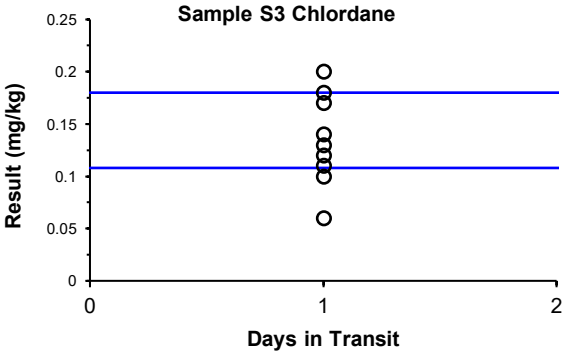


Figure 97 S3 Chlordane Results vs Transit Days

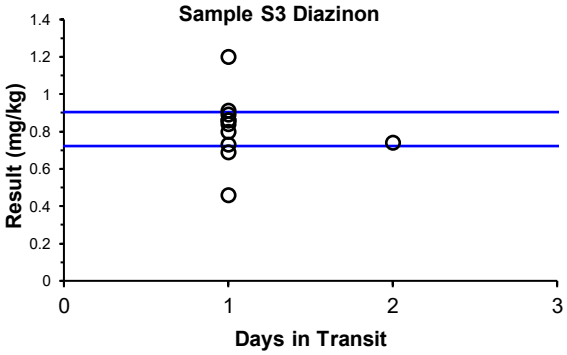


Figure 98 S3 Diazinon Results vs Transit Days

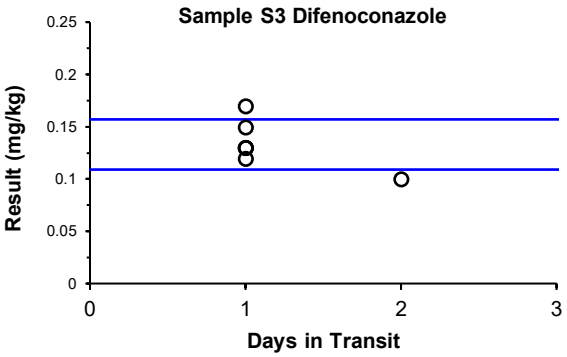


Figure 99 S3 Difenoconazole Results vs Transit Days

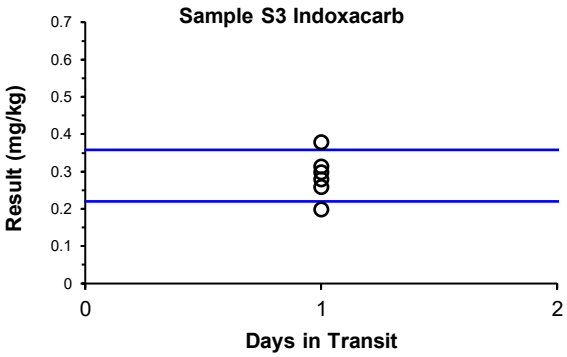


Figure 100 S3 Indoxacarb Results vs Transit Days

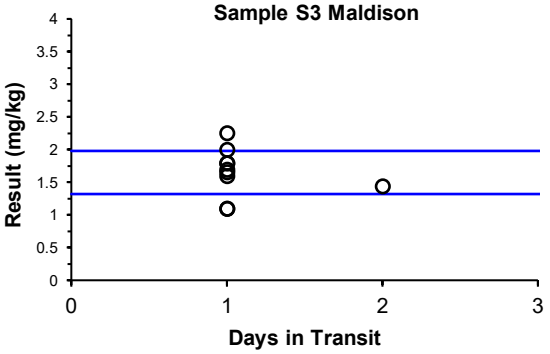


Figure 101 S3 Maldison Results vs Transit Days

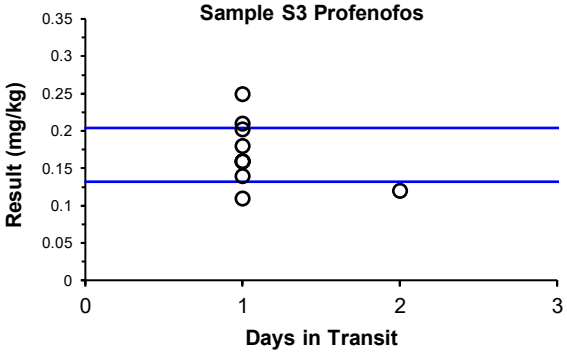


Figure 102 S3 Profenofos Results vs Transit Days

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

A3.1 Robust Average and Associated Uncertainty

Robust averages were calculated using the procedure described in ISO 13528.[7] The associated uncertainties were evaluated 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 S3 profenofos is set out below in Table 44.

Table 44 Uncertainty of Robust Average for Sample S3 Profenofos

Number of results (p)	10
Robust Average	0.168 mg/kg
$S_{rob\ av}$	0.045 mg/kg
$u_{rob\ av}$	0.018 mg/kg
k	2
$U_{rob\ av}$	0.036 mg/kg

Therefore, the robust average for Sample S1 profenofos is 0.168 ± 0.036 mg/kg.

A3.2 z-Score and E_n-Score Calculation

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

A worked example for the result reported by Laboratory 6 for Sample S1 indoxacarb is set out below in Table 45.

Table 45 z-Score and E_n-Score for Sample S1 Indoxacarb Result Reported by Laboratory 6

Participant Result (mg/kg)	Assigned Value (mg/kg)	Standard Deviation for Proficiency Assessment	z-Score	E_n-Score
0.28 ± 0.084	0.256 ± 0.043	15% as CV, or: 0.15 × 0.256 = 0.0384 mg/kg	$z = \frac{0.28 - 0.256}{0.0384} = 0.63$	$E_n = \frac{0.28 - 0256}{\sqrt{0.0.84^2 + 0.043^2}} = 0.25$

APPENDIX 4 PARTICIPANTS' TEST METHODS

A4.1 METHODOLOGY FOR S1 TOMATO

Table 46 Measurement Methods and Instrument Techniques for Abamectin

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	LC-MS	Pirimicarb D 6
8	10	No	Solid-Liquid (Mechanical Agitation)	Acidified acetonitrile	10 mL, 1 step	1	NA	NA	QuEChERS (dSPE)	LC-MS/MS	yes, atrazine-D5
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30				LC-MS/MS	Yes - Atrazine-D5, Carabaryl-D7, Diuron-D6
12	5	QUECHER	Acetonitrile	PSA	LC-MS/MS						
16	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	LC-MS/MS	No
17	10	No	QuEChERS/ LLE/SPE	ACN	10	3	20	0	Filtration	LC-MS/MS	TPP

Table 47 Measurement Methods and Instrument Techniques for Acephate

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
2	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	5	25		QuEChERS (dSPE)	LC-MS/MS	Yes, TPP
4	20	No	Solid-Liquid (Mechanical Agitation)	DCM,Hex, Acetone	100mls, 3 steps	60	45	30	Filtration	LC-MS/MS	no
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	LC-MS	Pirimicarb D 6
6	10	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	LC-MS/MS	No
8	10	No	Solid-Liquid (Mechanical Agitation)	Acidified acetonitrile	10 mL, 1 step	1	NA	NA	QuEChERS (dSPE)	LC-MS/MS	yes, atrazine-D5
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30				LC-MS/MS	Yes - Atrazine-D5, Carabaryl-D7, Diuron-D6
12	5	QUECHER	Acetonitrile	PSA	LC-MS/MS						
16	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	LC-MS/MS	No
17	10	No	QuEChERS/ LLE/SPE	ACN	10	3	20	0	Filtration	LC-MS/MS	TPP

Table 48 Measurement Methods and Instrument Techniques for Buprofezin

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
1	10	NO	Solid-Liquid (Mechanical Agitation)	ACETONITRILE	100 mL, 1 step	2	40	5	SPE (Reverse Phase)	GC-MS	NO
2	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	5	25		QuEChERS (dSPE)	LC-MS/MS	Yes, TPP
3	10	No	QuEChERS	Acetonitrile	10 mL, 1 step	20			QuEChERS (dSPE)	LC-MS/MS	No
4	20	No	Solid-Liquid (Mechanical Agitation)	DCM,Hex, Acetone	100mls, 3 steps	60	45	30	Filtration	GC-MS/MS	no
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	LC-MS	Pirimicarb D 6
6	10	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	LC-MS/MS	No
7	15	Yes, before clean-up	QuEChERS	Acetonitrile	15 mL, 6 steps	90	38	15	PSA	LC-MS/MS	No
8	10	No	Solid-Liquid (Mechanical Agitation)	Acidified acetonitrile	10 mL, 1 step	1	NA	NA	QuEChERS (dSPE)	LC-MS/MS	yes, atrazine-D5
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30				LC-MS/MS	Yes - Atrazine-D5, Carabaryl-D7, Diuron-D6

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
11	10	No	QuEChERS Salt	Acetonitrile	10 mL, 1 step	30	20	10	PSA/Carbon	GC-MS	No
12	5	QUECHER	Acetonitrile	PSA	GC-MS/MS						
16	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	LC-MS/MS	No
17	10	No	QuEChERS/ LLE/SPE	ACN	10	3	20	0	QuEChERS (dSPE)	GC-MS/MS	TPP

Table 49 Measurement Methods and Instrument Techniques for Endosulfan Sulfate

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
1	10	NO	Solid-Liquid (Mechanical Agitation)	ACETONITRILE	100 mL, 1 step	2	40	5	SPE (Reverse Phase)	GC-MS	NO
2	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	5	25		QuEChERS (dSPE)	GC-MS/MS	Yes, TPP
3	10	No	QuEChERS	Acetonitrile	10 mL, 1 step	20			QuEChERS (dSPE)	GC-MS	No
4	20	No	Solid-Liquid (Mechanical Agitation)	DCM,Hex, Acetone	100mls, 3 steps	60	45	30	Filtration	GC-ECD	no

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	GC-MS	Chlorpyrifos D10
6	10	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	GC-MS/MS	Yes, Triphenyl Phosphate
8	10	No	Solid-Liquid (Mechanical Agitation)	Acidified acetonitrile	10 mL, 1 step	1	NA	NA	QuEChERS (dSPE)	GC-MS/MS	yes, atrazine-D5
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30			QuEChERS (dSPE)	GC-MS/MS	Yes - Tributyl phosphate, 2,4,5,6-tetrachloro-m-xylene
10	5	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10mL,1 step	3	40	10	QuEChERS (dSPE)	GC-MS/MS	Naphtalene-D8
11	10	No	QuEChERS Salt	Acetonitrile	10 mL, 1 step	30	20	10	PSA/Carbon	GC-MS	No
12	5	QUECHER	Acetonitrile	PSA	GC-MS/MS						
13	10	No	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30	N/A	N/A	QuEChERS (dSPE)150mg PSA, 900mg MgSO4	GC-ECD	No
14	10	No	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	10	20	N/A	QuEChERS (dSPE)	GC-ECD	No

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
16	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	GC-MS/MS	Yes,TPP
17	10	No	QuEChERS/ LLE/SPE	ACN	10	3	20	0	QuEChERS (dSPE)	GC-MS/MS	TPP

Table 50 Measurement Methods and Instrument Techniques for Fenvalerate

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
1	10	NO	Solid-Liquid (Mechanical Agitation)	ACETONIT RILE	100 mL, 1 step	2	40	5	SPE (Reverse Phase)	GC-MS	NO
2	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	5	25		QuEChERS (dSPE)	GC-MS/MS	Yes, TPP
3	10	No	QuEChERS	Acetonitrile	10 mL, 1 step	20			QuEChERS (dSPE)	GC-MS	No
4	20	No	Solid-Liquid (Mechanical Agitation)	DCM,Hex, Acetone	100mls, 3 steps	60	45	30	Filtration	GC-MS/MS	no
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	GC-MS	Chlorpyrifos D10

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
6	10	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	GC-MS/MS	Yes, Triphenyl Phosphate
7	15	Yes, before clean-up	QuEChERS	Acetonitrile	15 mL, 6 steps	90	38	15	PSA	LC-MS/MS	No
8	10	No	Solid-Liquid (Mechanical Agitation)	Acidified acetonitrile	10 mL, 1 step	1	NA	NA	QuEChERS (dSPE)	GC-MS/MS	yes, atrazine-D5
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30			QuEChERS (dSPE)	GC-MS/MS	Yes - Tributyl phosphate, 2,4,5,6-tetrachloro-m-xylene
10	5	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10mL,1 step	3	40	10	QuEChERS (dSPE)	GC-MS/MS	Naphtalene-D8
11	10	No	QuEChERS Salt	Acetonitrile	10 mL, 1 step	30	20	10	PSA/Carbon	GC-MS	No
12	5	QUECHER	Acetonitrile	PSA	GC-MS/MS						
13	10	No	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30	N/A	N/A	QuEChERS (dSPE) 150mg PSA, 900mg MgSO4	GC-ECD	No
14	10	No	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	10	20	N/A	QuEChERS (dSPE)	GC-ECD	No

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
16	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	GC-MS/MS	Yes,TPP
17	10	No	QuEChERS/ LLE/SPE	ACN	10	3	20	0	QuEChERS (dSPE)	GC-MS/MS	TPP

Table 51 Measurement Methods and Instrument Techniques for Imidacloprid

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
2	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	5	25		QuEChERS (dSPE)	LC-MS/MS	Yes, TPP
3	10	No	QuEChERS	Acetonitrile	10 mL, 1 step	20			QuEChERS (dSPE)	LC-MS/MS	No
4	20	No	Solid-Liquid (Mechanical Agitation)	DCM,Hex, Acetone	100mls, 3 steps	60	45	30	Filtration	LC-MS/MS	no
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	LC-MS	Pirimicarb D 6
6	10	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	LC-MS/MS	No

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
8	10	No	Solid-Liquid (Mechanical Agitation)	Acidified acetonitrile	10 mL, 1 step	1	NA	NA	QuEChERS (dSPE)	LC-MS/MS	yes, atrazine-D5
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30				LC-MS/MS	Yes - Atrazine-D5, Carabaryl-D7, Diuron-D6
10	5	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10mL,1 step	3	40	10	QuEChERS (dSPE)	LC-MS/MS	Atrazine D5, diazinon D10
12	5	QUECHER	Acetonitrile	PSA	LC-MS/MS						
16	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	LC-MS/MS	No
17	10	No	QuEChERS/ LLE/SPE	ACN	10	3	20	0	Filtration	LC-MS/MS	TPP

Table 52 Measurement Methods and Instrument Techniques for Indoxacarb

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
1	10	NO	Solid-Liquid (Mechanical Agitation)	ACETONITRILE	100 mL, 1 step	2	40	5	SPE (Reverse Phase)	GC-MS	NO
3	10	No	QuEChERS	Acetonitrile	10 mL, 1 step	20			QuEChERS (dSPE)	LC-MS/MS	No

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
4	20	No	Solid-Liquid (Mechanical Agitation)	DCM,Hex, Acetone	100mls, 3 steps	60	45	30	Filtration	GC-MS/MS	no
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	LC-MS	Pirimicarb D 6
6	10	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	LC-MS/MS	No
7	15	Yes, before clean-up	QuEChERS	Acetonitrile	15 mL, 6 steps	90	38	15	PSA	LC-MS/MS	No
8	10	No	Solid-Liquid (Mechanical Agitation)	Acidified acetonitrile	10 mL, 1 step	1	NA	NA	QuEChERS (dSPE)	LC-MS/MS	yes, atrazine-D5
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30				LC-MS/MS	Yes - Atrazine-D5, Carabaryl-D7, Diuron-D6
11	10	No	QuEChERS Salt	Acetonitrile	10 mL, 1 step	30	20	10	PSA/Carbon	GC-MS	No
12	5	QUECHER	Acetonitrile	PSA	GC-MS/MS						
14	10	No	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	10	20	N/A	QuEChERS (dSPE)	GC-ECD	No
16	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	LC-MS/MS	No

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
17	10	No	QuEChERS/ LLE/SPE	ACN	10	3	20	0	Filtration	LC-MS/MS	TPP

Table 53 Measurement Methods and Instrument Techniques for Methomyl

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
2	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	5	25		QuEChERS (dSPE)	LC-MS/MS	Yes, TPP
3	10	No	QuEChERS	Acetonitrile	10 mL, 1 step	20			QuEChERS (dSPE)	LC-MS/MS	No
4	20	No	Solid-Liquid (Mechanical Agitation)	DCM,Hex, Acetone	100mls, 3 steps	60	45	30	Filtration	LC-MS/MS	no
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	LC-MS	Pirimicarb D 6
6	10	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	LC-MS/MS	No
7	15	Yes, before clean-up	QuEChERS	Acetonitrile	15 mL, 6 steps	90	38	15	PSA	LC-MS/MS	No
8	10	No	Solid-Liquid (Mechanical Agitation)	Acidified acetonitrile	10 mL, 1 step	1	NA	NA	QuEChERS (dSPE)	LC-MS/MS	yes, atrazine-D5

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30				LC-MS/MS	Yes - Atrazine-D5, Carabaryl-D7, Diuron-D6
12	5	QUECHER	Acetonitrile	PSA	LC-MS/MS						
16	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	LC-MS/MS	No
17	10	No	QuEChERS/ LLE/SPE	ACN	10	3	20	0	Filtration	LC-MS/MS	TPP

Table 54 Additional Information for Sample S1

Lab. Code	Participant's Comments
4	Foritifed samples run in parallel with samples. Note the uncertainty on methomyl in this tomato sample is high due to widely varying repeat analysis results between initial screen and repeat analysis
7	Chlorothalonil, Cypermethrin, Dicofol: Not accredited. Analysed via GC-MS/MS.
9	Abamectin analysed as "avermectin b1a". Fenvalerate reported as sum of fenvalerate and esfenvalerate.
13	The reported result is based on a single analysis and was not corrected for recovery. The expanded measurement uncertainty (k = 2) was estimated based on the laboratory's method validation data.

A4.2 METHODOLOGY FOR S2 BLUEBERRY

Table 55 Measurement Methods and Instrument Techniques for Bifenthrin

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
1	10	NO	Solid-Liquid (Mechanical Agitation)	ACETONITRILE	100 mL, 1 step	2	40	5	SPE (Reverse Phase)	GC-MS	NO
2	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	5	25		QuEChERS (dSPE)	GC-MS/MS	Yes, TPP
3	10	No	QuEChERS	Acetonitrile	10 mL, 1 step	20			QuEChERS (dSPE)	GC-MS	No
4	20	No	Solid-Liquid (Mechanical Agitation)	DCM,Hex, Acetone	100mls, 3 steps	60	45	30	Filtration	GC-MS/MS	no
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	GC-MS	Chlorpyrifos D10
6	10	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	GC-MS/MS	Yes, Triphenyl Phosphate
7	15	Yes, before clean-up	QuEChERS	Acetonitrile	15 mL, 6 steps	90	38	15	PSA	GC-MS/MS	No

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
8	10	No	Solid-Liquid (Mechanical Agitation)	Acidified acetonitrile	10 mL, 1 step	1	NA	NA	QuEChERS (dSPE)	LC-MS/MS	yes, atrazine-D5
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30			QuEChERS (dSPE)	GC-MS/MS	Yes - Tributyl phosphate, 2,4,5,6-tetrachloro-m-xylene
10	5	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10mL,1 step	3	40	10	QuEChERS (dSPE)	GC-MS/MS	Naphtalene-D8
11	10	No	QuEChERS Salt	Acetonitrile	10 mL, 1 step	30	20	10	PSA/Carbon	GC-MS	No
12	5	QUECHER	Acetonitrile	PSA	GC-MS/MS						
13	10	No	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30	N/A	N/A	QuEChERS (dSPE) 150mg PSA, 900mg MgSO4, 150mg C18, 45mg GCB	GC-ECD	No
14	10	No	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	10	20	N/A	QuEChERS (dSPE)	GC-ECD	No
16	10	Yes, before clean-up	Solid-Liquid	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	GC-MS/MS	Yes,TPP

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
			(Mechanical Agitation)								

Table 56 Measurement Methods and Instrument Techniques for Chlorpyrifos

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
1	10	NO	Solid-Liquid (Mechanical Agitation)	ACETONITRILE	100 mL, 1 step	2	40	5	SPE (Reverse Phase)	GC-MS	NO
2	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	5	25		QuEChERS (dSPE)	GC-MS/MS	Yes, TPP
3	10	No	QuEChERS	Acetonitrile	10 mL, 1 step	20			QuEChERS (dSPE)	GC-MS	No
4	20	No	Solid-Liquid (Mechanical Agitation)	DCM,Hex, Acetone	100mls, 3 steps	60	45	30	Filtration	GC-MS/MS	no
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	GC-MS	Chlorpyrifos D10

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
6	10	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	GC-MS/MS	Yes, Triphenyl Phosphate
7	15	Yes, before clean-up	QuEChERS	Acetonitrile	15 mL, 6 steps	90	38	15	PSA	LC-MS/MS	No
8	10	No	Solid-Liquid (Mechanical Agitation)	Acidified acetonitrile	10 mL, 1 step	1	NA	NA	QuEChERS (dSPE)	GC-MS/MS	yes, atrazine-D5
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30			QuEChERS (dSPE)	GC-MS/MS	Yes - Tributyl phosphate, 2,4,5,6-tetrachloro-m-xylene
10	5	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10mL,1 step	3	40	10	QuEChERS (dSPE)	GC-MS/MS	Naphtalene-D8
11	10	No	QuEChERS Salt	Acetonitrile	10 mL, 1 step	30	20	10	PSA/Carbon	GC-FPD	No
12	5	QUECHER	Acetonitrile	PSA	GC-MS/MS						
13	10	No	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30	N/A	N/A	QuEChERS (dSPE) 150mg PSA, 900mg MgSO4, 150mg C18, 45mg GCB	GC-FPD	No

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
14	10	No	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	10	20	N/A	QuEChERS (dSPE)	GC-ECD	No
16	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	GC-MS/MS	Yes,TPP

Table 57 Measurement Methods and Instrument Techniques for Cyprodinil

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
2	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	5	25		QuEChERS (dSPE)	LC-MS/MS	Yes, TPP
4	20	No	Solid-Liquid (Mechanical Agitation)	DCM,Hex, Acetone	100mls, 3 steps	60	45	30	Filtration	LC-MS/MS	no
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	LC-MS	Pirimicarb D 6
6	10	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	LC-MS/MS	No
7	15	Yes, before clean-up	QuEChERS	Acetonitrile	15 mL, 6 steps	90	38	15	PSA	LC-MS/MS	No

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
8	10	No	Solid-Liquid (Mechanical Agitation)	Acidified acetonitrile	10 mL, 1 step	1	NA	NA	QuEChERS (dSPE)	LC-MS/MS	yes, atrazine-D5
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30				LC-MS/MS	Yes - Atrazine-D5, Carabaryl-D7, Diuron-D6
12	5	QUECHER	Acetonitrile	PSA	GC-MS/MS						
16	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	LC-MS/MS	No

Table 58 Measurement Methods and Instrument Techniques for Dimethoate

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
1	10	NO	Solid-Liquid (Mechanical Agitation)	ACETONITRILE	100 mL, 1 step	2	40	5	SPE (Reverse Phase)	GC-MS	NO
2	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	5	25		QuEChERS (dSPE)	LC-MS/MS	Yes, TPP
3	10	No	QuEChERS	Acetonitrile	10 mL, 1 step	20			QuEChERS (dSPE)	GC-MS	No

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
4	20	No	Solid-Liquid (Mechanical Agitation)	DCM,Hex, Acetone	100mls, 3 steps	60	45	30	Filtration	LC-MS/MS	no
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	LC-MS	Pirimicarb D 6
6	10	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	GC-MS/MS	Yes, Triphenyl Phosphate
7	15	Yes, before clean-up	QuEChERS	Acetonitrile	15 mL, 6 steps	90	38	15	PSA	LC-MS/MS	No
8	10	No	Solid-Liquid (Mechanical Agitation)	Acidified acetonitrile	10 mL, 1 step	1	NA	NA	QuEChERS (dSPE)	GC-MS/MS	yes, atrazine-D5
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30				LC-MS/MS	Yes - Atrazine-D5, Carabaryl-D7, Diuron-D6
10	5	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10mL,1 step	3	40	10	QuEChERS (dSPE)	LC-MS/MS	Atrazine D5, diazinon D10
11	10	No	QuEChERS Salt	Acetonitrile	10 mL, 1 step	30	20	10	PSA/Carbon	GC-FPD	No

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
12	5	QUECHER	Acetonitrile	PSA	LC-MS/MS						
13	10	No	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30	N/A	N/A	QuEChERS (dSPE) 150mg PSA, 900mg MgSO4, 150mg C18, 45mg GCB	GC-FPD	No
14	15	No	Solid-Liquid (Mechanical Agitation)	ACN	15 mL, 1 step	10	20	5	QuEChERS (SPE)	GC-FPD	No
16	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	LC-MS/MS	No

Table 59 Measurement Methods and Instrument Techniques for Imidacloprid

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
2	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	5	25		QuEChERS (dSPE)	LC-MS/MS	Yes, TPP
3	10	No	QuEChERS	Acetonitrile	10 mL, 1 step	20			QuEChERS (dSPE)	LC-MS/MS	No

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	LC-MS	Pirimicarb D 6
6	10	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	LC-MS/MS	No
8	10	No	Solid-Liquid (Mechanical Agitation)	Acidified acetonitrile	10 mL, 1 step	1	NA	NA	QuEChERS (dSPE)	LC-MS/MS	yes, atrazine-D5
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30				LC-MS/MS	Yes - Atrazine-D5, Carabaryl-D7, Diuron-D6
10	5	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10mL,1 step	3	40	10	QuEChERS (dSPE)	LC-MS/MS	Atrazine D5, diazinon D10
12	5	QUECHER	Acetonitrile	PSA	LC-MS/MS						
16	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	LC-MS/MS	No

Table 60 Measurement Methods and Instrument Techniques for Maldison

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
1	10	NO	Solid-Liquid (Mechanical Agitation)	ACETONITRILE	100 mL, 1 step	2	40	5	SPE (Reverse Phase)	GC-MS	NO
2	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	5	25		QuEChERS (dSPE)	GC-MS/MS	Yes, TPP
3	10	No	QuEChERS	Acetonitrile	10 mL, 1 step	20			QuEChERS (dSPE)	GC-MS	No
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	GC-MS	Chlorpyrifos D10
6	10	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	GC-MS/MS	Yes, Triphenyl Phosphate
7	15	Yes, before clean-up	QuEChERS	Acetonitrile	15 mL, 6 steps	90	38	15	PSA	LC-MS/MS	No
8	10	No	Solid-Liquid (Mechanical Agitation)	Acidified acetonitrile	10 mL, 1 step	1	NA	NA	QuEChERS (dSPE)	GC-MS/MS	yes, atrazine-D5
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30			QuEChERS (dSPE)	GC-MS/MS	Yes - Tributyl phosphate, 2,4,5,6-tetrachloro-m-xylene
10	5	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10mL,1 step	3	40	10	QuEChERS (dSPE)	GC-MS/MS	Naphtalene-D8

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
11	10	No	QuEChERS Salt	Acetonitrile	10 mL, 1 step	30	20	10	PSA/Carbon	GC-FPD	No
12	5	QUECHER	Acetonitrile	PSA	GC-MS/MS						
13	10	No	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30	N/A	N/A	QuEChERS (dSPE) 150mg PSA, 900mg MgSO4, 150mg C18, 45mg GCB	GC-FPD	No
14	15	No	Solid-Liquid (Mechanical Agitation)	ACN	15 mL, 1 step	10	20	5	QuEChERS (SPE)	GC-FPD	No
16	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	LC-MS/MS	No

Table 61 Measurement Methods and Instrument Techniques for Methomyl

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
2	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	5	25		QuEChERS (dSPE)	LC-MS/MS	Yes, TPP
3	10	No	QuEChERS	Acetonitrile	10 mL, 1 step	20			QuEChERS (dSPE)	LC-MS/MS	No

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
4	20	No	Solid-Liquid (Mechanical Agitation)	DCM,Hex, Acetone	100mls, 3 steps	60	45	30	Filtration	LC-MS/MS	no
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	LC-MS	Pirimicarb D 6
6	10	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	LC-MS/MS	No
7	15	Yes, before clean-up	QuEChERS	Acetonitrile	15 mL, 6 steps	90	38	15	PSA	LC-MS/MS	No
8	10	No	Solid-Liquid (Mechanical Agitation)	Acidified acetonitrile	10 mL, 1 step	1	NA	NA	QuEChERS (dSPE)	LC-MS/MS	yes, atrazine-D5
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30				LC-MS/MS	Yes - Atrazine-D5, Carabaryl-D7, Diuron-D6
12	5	QUECHER	Acetonitrile	PSA	LC-MS/MS						
16	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	LC-MS/MS	No

Table 62 Measurement Methods and Instrument Techniques for Phosmet

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	LC-MS	Pirimicarb D 6
6	10	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	GC-MS/MS	Yes, Triphenyl Phosphate
8	10	No	Solid-Liquid (Mechanical Agitation)	Acidified acetonitrile	10 mL, 1 step	1	NA	NA	QuEChERS (dSPE)	LC-MS/MS	yes, atrazine-D5
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30			QuEChERS (dSPE)	GC-MS/MS	Yes - Tributyl phosphate, 2,4,5,6-tetrachloro-m-xylene
10	5	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10mL,1 step	3	40	10	QuEChERS (dSPE)	GC-MS/MS	Naphtalene-D8
12	5	QUECHER	Acetonitrile	PSA	LC-MS/MS						
16	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	LC-MS/MS	No

Table 63 Measurement Methods and Instrument Techniques for Thiometon

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
4	20	No	Solid-Liquid (Mechanical Agitation)	DCM,Hex, Acetone	100mls, 3 steps	60	45	30	Filtration	LC-MS/MS	no
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	LC-MS	Pirimicarb D 6
6	10	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	GC-MS/MS	Yes, Triphenyl Phosphate
12	5	QUECHER	Acetonitrile	PSA	GC-MS/MS						
16	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	GC-MS/MS	Yes,TPP

Table 64 Additional Information for Sample S2

Lab. Code	Participant's Comments
1	Bifenthrin and Azoxystrobin detected in the controlled samples.
2	Azoxystrobin - 0.04 mg/kg, Boscalid - 0.02 mg/kg,
4	Foritifed samples run in parallel with samples. Azoxystrobin detected in sample and blank at 0.02, Note Thiometon was looked for, and detected, but due to unreliability of old reference standard and repeatability issues, was marked as not tested.
6	Thiometon sulfoxide was detected, but did not report with Thiometon as requested as per PT instruction.
7	Bifenthrin, Cypermethrin: Not accredited. Analysed via GC-MS/MS.
9	Abamectin analysed as "avermectin b1a". Azoxystrobin incurred residue 0.036mg/kg. Bifenthrin incurred residue. Boscalid incurred residue 0.015 mg/kg.

Lab. Code	Participant's Comments
12	*Blank Blueberry Detected Bifenthrin 0.019 mg/kg (incurred in unspiked sample)
13	Bifenthrin was detected in US2. Dimethoate and malathion results were recovery-corrected based on validated method data; other analytes were reported without correction (expanded uncertainty, k = 2).
14	Incurred analyte detected in unspiked blueberry sample is Bifenthrin.
16	Unspiked sample contains residue of Bifenthrin and Imidacloprid.

A4.3 METHODOLOGY FOR S3 HEMP FLOUR

Table 65 Measurement Methods and Instrument Techniques for AMPA

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
2	2.5	No	Solid-Liquid (Mechanical Agitation)	Methanol	5 mL, 1 step	15	25		SPE (QPP)	LC-MS/MS	No
5	10	No	Solid-Liquid (Sonication)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	LC-MS	Pirimicarb D 6
9	10	No	Solid-Liquid (Mechanical Agitation)	0.6M KOH	5ml, 1 step	30				LC-MS/MS	Yes - Glyphosate-1,2-13C2 15N, AMPA-13C-15N, FL-Glufosinate
10	0.5	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	water	10mL, 1 step	3			Filtration	LC-MS/MS	13C 15N AMPA, 13C 15N Glyphosate
12	5	QuPPe	Methanol/water		LC-MS/MS	Glyphosate/ maleic					
15	0.5	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	0.1 M HCl	10 mL, 1 step	60			Filtration	LC-MS/MS	Yes, multiple ISTDs.

Table 66 Measurement Methods and Instrument Techniques for Azoxystrobin

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
1	2	NO	Solid-Liquid (Mechanical Agitation)	ACETONITRILE	10 mL, 1 step	2	40	5	SPE (Reverse Phase)	GC-MS	NO
2	2	No	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	5	25		QuEChERS (dSPE)	LC-MS/MS	Yes, TPP
4	20	No	Solid-Liquid (Mechanical Agitation)	DCM,Hex, Acetone	100mls, 3 steps	60	45	30	Filtration	LC-MS/MS	no
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	LC-MS	Pirimicarb D 6
6	2	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	LC-MS/MS	No
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30				LC-MS/MS	Yes - Atrazine-D5, Carabaryl-D7, Diuron-D6
10	0.5	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10mL,1 step	3	40	10	QuEChERS (dSPE)	LC-MS/MS	Atrazine D5, diazinin D10
12	5	QUECHER	Acetonitrile	PSA	LC-MS/MS						
15	1	Yes, after clean-up	Solid-Liquid (Mechanical Agitation)	Acetronitrile	10mL, 2steps	120	Room temperature.	No concentration.	QuEChERS (dSPE)	LC-MS/MS	Yes, surrogate acted as ISTD.

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
16	2	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	LC-MS/MS	No

Table 67 Measurement Methods and Instrument Techniques for Chlordane

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
2	2	No	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	5	25		QuEChERS (dSPE)	GC-MS/MS	Yes, TPP
4	20	No	Solid-Liquid (Mechanical Agitation)	DCM,Hex, Acetone	100mls, 3 steps	60	45	30	Filtration	GC-ECD	no
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	GC-MS	Chlorpyrifos D10
6	2	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	GC-MS/MS	Yes, Triphenyl Phosphate
8	1	No	Solid-Liquid (Mechanical Agitation)	1:1 acidified Acetonitrile: water	20 mL, 1 step	1	NA	NA	QuEChERS (dSPE)	GC-MS/MS	No
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30			QuEChERS (dSPE)	GC-MS/MS	Yes - Tributyl phosphate, 2,4,5,6-

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
											tetrachloro-m-xylene
10	1	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10mL,1 step	3	40	10	QuEChERS (dSPE)	GC-MS/MS	Naphtalene-D8
12	5	QUECHER	Acetonitrile	PSA	GC-MS/MS						
15	1	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetronitrile	20mL, 1step	150	Room temperature.	No concentration.		GC-MS/MS	Yes, multiple ISTDs.
16	2	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	GC-MS/MS	Yes, TPP

Table 68 Measurement Methods and Instrument Techniques for Cypermethrin

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
1	2	NO	Solid-Liquid (Mechanical Agitation)	ACETONITRILE	10 mL, 1 step	2	40	5	SPE (Reverse Phase)	GC-ECD	NO
2	2	No	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	5	25		QuEChERS (dSPE)	GC-MS/MS	Yes, TPP
4	20	No	Solid-Liquid (Mechanical Agitation)	DCM,Hex, Acetone	100mls, 3 steps	60	45	30	Filtration	GC-MS/MS	no

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	GC-MS	Chlorpyrifos D10
6	2	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	GC-MS/MS	Yes, Triphenyl Phosphate
8	1	No	Solid-Liquid (Mechanical Agitation)	1:1 acidified Acetonitrile: water	20 mL, 1 step	1	NA	NA	QuEChERS (dSPE)	GC-MS/MS	No
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30			QuEChERS (dSPE)	GC-MS/MS	Yes - Tributyl phosphate, 2,4,5,6-tetrachloro-m-xylene
10	1	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10mL,1 step	3	40	10	QuEChERS (dSPE)	GC-MS/MS	Naphtalene-D8
12	5	QUECHER	Acetonitrile	PSA	GC-MS/MS						
15	1	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetronitrile	20mL, 1step	150	Room temperature.	No concentration.		GC-MS/MS	Yes, multiple ISTDs.
16	2	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	GC-MS/MS	Yes, TPP

Table 69 Measurement Methods and Instrument Techniques for Diazinon

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
1	2	NO	Solid-Liquid (Mechanical Agitation)	ACETONITRILE	10 mL, 1 step	2	40	5	SPE (Reverse Phase)	GC-FPD	NO
2	2	No	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	5	25		QuEChERS (dSPE)	GC-MS/MS	Yes, TPP
4	20	No	Solid-Liquid (Mechanical Agitation)	DCM,Hex, Acetone	100mls, 3 steps	60	45	30	Filtration	LC-MS/MS	no
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	LC-MS	Pirimicarb D 6
6	2	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	GC-MS/MS	Yes, Triphenyl Phosphate
8	1	No	Solid-Liquid (Mechanical Agitation)	1:1 acidified Acetonitrile: water	20 mL, 1 step	1	NA	NA	QuEChERS (dSPE)	GC-MS/MS	No
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30			QuEChERS (dSPE)	GC-MS/MS	Yes - Tributyl phosphate, 2,4,5,6-tetrachloro-m-xylene
10	0.5	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10mL,1 step	3	40	10	QuEChERS (dSPE)	LC-MS/MS	Atrazine D5, diazinin D10
12	5	QUECHER	Acetonitrile	PSA	GC-MS/MS						

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
15	1	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetronitrile	20mL, 1step	150	Room temperature.	No concentration.		GC-MS/MS	Yes, multiple ISTDs.
16	2	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	LC-MS/MS	No

Table 70 Measurement Methods and Instrument Techniques for Difenoconazole

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
1	2	NO	Solid-Liquid (Mechanical Agitation)	ACETONITRILE	10 mL, 1 step	2	40	5	SPE (Reverse Phase)	GC-ECD	NO
2	2	No	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	5	25		QuEChERS (dSPE)	LC-MS/MS	Yes, TPP
4	20	No	Solid-Liquid (Mechanical Agitation)	DCM,Hex, Acetone	100mls, 3 steps	60	45	30	Filtration	LC-MS/MS	no
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	GC-MS	Chlorpyrifos D10
6	2	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	LC-MS/MS	No

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30				LC-MS/MS	Yes - Atrazine-D5, Carabaryl-D7, Diuron-D6
12	5	QUECHER	Acetonitrile	PSA	GC-MS/MS						
16	2	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	LC-MS/MS	No

Table 71 Measurement Methods and Instrument Techniques for Indoxacarb

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
4	20	No	Solid-Liquid (Mechanical Agitation)	DCM,Hex, Acetone	100mls, 3 steps	60	45	30	Filtration	LC-MS/MS	no
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	LC-MS	Pirimicarb D 6
6	2	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	LC-MS/MS	No
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30				LC-MS/MS	Yes - Atrazine-D5, Carabaryl-D7, Diuron-D6
12	5	QUECHER	Acetonitrile	PSA	GC-MS/MS						
16	2	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	LC-MS/MS	No

Table 72 Measurement Methods and Instrument Techniques for Maldison

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
1	2	NO	Solid-Liquid (Mechanical Agitation)	ACETONITRILE	10 mL, 1 step	2	40	5	SPE (Reverse Phase)	GC-FPD	NO

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
2	2	No	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	5	25		QuEChERS (dSPE)	GC-MS/MS	Yes, TPP
4	20	No	Solid-Liquid (Mechanical Agitation)	DCM,Hex, Acetone	100mls, 3 steps	60	45	30	Filtration	GC-MS/MS	no
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	GC-MS	Chlorpyrifos D10
6	2	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	GC-MS/MS	Yes, Triphenyl Phosphate
8	1	No	Solid-Liquid (Mechanical Agitation)	1:1 acidified Acetonitrile: water	20 mL, 1 step	1	NA	NA	QuEChERS (dSPE)	GC-MS/MS	No
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30				LC-MS/MS	Yes - Atrazine-D5, Carabaryl-D7, Diuron-D6
10	1	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10mL,1 step	3	40	10	QuEChERS (dSPE)	GC-MS/MS	Naphtalene-D8
12	5	QUECHER	Acetonitrile	PSA	GC-MS/MS						
15	1	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetronitrile	20mL, 1step	150	Room temperature.	No concentration.		GC-MS/MS	Yes, multiple ISTDs.

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
16	2	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	LC-MS/MS	No

Table 73 Measurement Methods and Instrument Techniques for Profenofos

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
1	2	NO	Solid-Liquid (Mechanical Agitation)	ACETONIT RILE	10 mL, 1 step	2	40	5	SPE (Reverse Phase)	GC-FPD	NO
2	2	No	Solid-Liquid (Mechanical Agitation)	ACN	10 mL, 1 step	5	25		QuEChERS (dSPE)	GC-MS/MS	Yes, TPP
4	20	No	Solid-Liquid (Mechanical Agitation)	DCM,Hex, Acetone	100mls, 3 steps	60	45	30	Filtration	GC-MS/MS	no
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	LC-MS	Pirimicarb D 6
6	2	No	Solid-Liquid (Mechanical Agitation)	1 % Acetic Acid in Acetronitile	10 mL, 1 step	5	NA	NA	QuEChERS (dSPE)	GC-MS/MS	Yes, Triphenyl Phosphate
8	1	No	Solid-Liquid (Mechanical Agitation)	1:1 acidified Acetonitrile: water	20 mL, 1 step	1	NA	NA	QuEChERS (dSPE)	GC-MS/MS	No

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
9	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10 mL, 1 step	30			QuEChERS (dSPE)	GC-MS/MS	Yes - Tributyl phosphate, 2,4,5,6-tetrachloro-m-xylene
10	1	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10mL,1 step	3	40	10	QuEChERS (dSPE)	GC-MS/MS	Naphtalene-D8
12	5	QUECHER	Acetonitrile	PSA	GC-MS/MS						
15	1	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetronitrile	20mL, 1step	150	Room temperature.	No concentration.		GC-MS/MS	Yes, multiple ISTDs.
16	2	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	Acetonitrile	10	5	4	5	QuEChERS (dSPE)	GC-MS/MS	Yes, TPP

Table 74 Additional Information for Sample S3

Lab. Code	Participant's Comments
4	Foritifed samples run in parallel with samples.
6	Hemp Flour is not accredited as no validation has been performed in this matrix so far.
9	Spinosad reported as sum of Spinosyn A and Spinosyn D. Chlordane Reported as sum of trans and cis chlordane.2,4-D incurred residue 0.011mg/kg.

A4.4 METHODOLOGY FOR S4 GARLIC

Table 75 Measurement Methods and Instrument Techniques for Maleic Hydrazide

Lab. Code	Sample Mass for Analysis (g)	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Clean-Up	Measurement Instrument	Were internal standards used? If yes, what internal standard?
5	10	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	acetonitrile	10mL, 1step	15 min	NA	NA	QuEChERS (dSPE)	LC-MS	Pirimicarb D 6
6	1	Yes, before clean-up	Solid-Liquid (Mechanical Agitation)	1% Formic Acid in Methanol	10,1 step	180	NA	NA	Filtration	LC-MS/MS	YES,Maleic Hydrazide-(D2)
12	5	QuPPe	Methanol/water		LC-MS/MS	Glyphosate/ maleic					
17	10	No	LLE/SPE	Methanol + 1% HCOOH	10	3	20	0	Filtration	LC-MS/MS	Maleic hydrazide- 13C4

APPENDIX 5 ACRONYMS AND ABBREVIATIONS

2,4-D	2,4-Dichlorophenoxyacetic acid
Ace	Acetone
ACN	Acetonitrile
AMPA	Aminomethylphosphonic Acid
AV	Assigned Value
CAC/GL	Codex Alimentarius Commission Guidelines
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
DCM	Dichloromethane
dSPE	Dispersive Solid Phase Extraction
ECD	Electron Capture Detection
FAO	Food and Agriculture Organization of the United Nations
FPD	Flame Photometric Detection
GC	Gas Chromatography
GCB	Graphitized Carbon Black
GUM	Guide to the expression of Uncertainty in Measurement
Hex	Hexane
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
JMPR	Joint FAO/WHO Meeting on Pesticide Residues
k	Coverage factor
LC	Liquid Chromatography
LLE	Liquid-Liquid Extraction
LOR	Limit of Reporting
Max	Maximum
Md	Median
MeOH	Methanol
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
NMIA	National Measurement Institute, Australia
NR	Not Reported
NS	Not Supplied
NT	Not Tested
PCV	Performance Coefficient of Variation
PSA	Primary/Secondary Amine
PT	Proficiency Testing
QuEChERS	Quick, Easy, Cheap, Effective, Rugged and Safe procedure
RA	Robust Average
Rec	Recovery
SANTE	Directorate-General for Health and Food Safety
SD	Standard Deviation
SDPA	Standard Deviation for Proficiency Assessment
SI	International System of Units
SLE	Solid-Liquid Extraction
SLE (MA)	Solid-Liquid Extraction (Mechanical Agitation)
SLE (S)	Solid-Liquid Extraction (Sonication)
SPE	Solid Phase Extraction
SS	Spiked Samples
SV	Spiked Value (or the formulated concentration)
WHO	World Health Organization

END OF REPORT