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National Measurement Institute

Proficiency Test Final Report AQA 23-09 Pesticides in Fruit, Vegetables & Herbs

September 2023

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

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SUMMARY

AQA 23-09 Pesticides in Fruit, Vegetables & Herbs commenced in May 2023. Twenty-one laboratories registered to participate, and all participants submitted results.

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

Of a possible 462 results, 271 numeric results (59%) were submitted. Of the remaining results, 45 results were a 'less than' value ($< x$) or Not Reported (NR), and 146 results were Not Tested (NT).

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

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

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

- *Assess the ability of participants to correctly identify pesticides in fruit, vegetables and herbs.*

Laboratories **1**, **4**, **6**, **7**, **9** and **17** reported numeric results for all 17 scored analytes.

Eleven participants did not report results for analytes that they tested for and were present in the test samples (total of 35 results).

For the samples prepared from organic matrices, one participant reported an analyte that was not spiked into the samples.

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

Of 217 results for which *z*-scores were calculated, 171 (79%) returned $|z| \leq 2.0$, indicating a satisfactory performance.

Of 217 results for which E_n-scores were calculated, 162 (75%) returned $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratory **1** achieved satisfactory *z*-scores and E_n-scores for all scored analytes.

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

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

Of 93 results assessed, 72 (77%) gave the correct compliance status with respect to the Australia New Zealand Food Standards Code.

Laboratory **4** returned the correct compliance status for all assessed analytes.

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

Participants used a variety of methods, and no significant trends with any particular sample preparation method or instrumental technique were evident. The most common methodology

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

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

Of 271 numeric results for the analytes of interest in this study, 244 (90%) were reported with an associated expanded measurement uncertainty. The magnitude of the reported uncertainties was within the range 3.4% to 250000% relative; some participants may have reported relative uncertainties instead of absolute uncertainties as requested for this study. A wide variety of procedures were used to estimate uncertainty.

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

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

1 INTRODUCTION

1.1 NMI Proficiency Testing Program

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

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

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

1.2 Study Aims

The aims of the study were to:

- assess the ability of participants to correctly identify pesticides in fruit, vegetables and herbs;
- compare the performances of participants and assess their accuracy in the measurement of pesticides in fruit, vegetables and herbs;
- assess the ability of participants to determine compliance of pesticides in fruit, vegetables and herbs against regulatory standards;
- evaluate participants' methods for the measurement of pesticides in fruit, vegetables and herbs;
- develop the practical application of traceability and measurement uncertainty; and
- produce materials that can be used in method validation and as control samples.

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

1.3 Study Conduct

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

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

2 STUDY INFORMATION

2.1 Selection of Pesticides and Matrices

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

Table 1 List of Possible Analytes

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

The spiked values for the samples and corresponding Australian maximum residue limits (MRLs) from the Australia New Zealand Food Standards Code,[5] are presented in Table 2. For matrix and analyte selection, consideration was given to:

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

Table 2 Spiked Values of Test Samples

Sample	Analyte	Spiked Value (mg/kg)	Uncertainty[a] (mg/kg)	MRL[b] (mg/kg)
S1 (Tomato)	Chlorothalonil	0.998	0.050	10
	Chlorpyrifos	0.821	0.041	T0.5
	Endosulfan sulfate	0.447	0.022	-
	Fenhexamid	0.502	0.025	T2
S2 (Bok Choy)	Bifenthrin	0.0167	0.0008	*0.01
	Indoxacarb	3.01	0.15	5[c]
	Iprodione	8.04	0.40	15

Sample	Analyte	Spiked Value (mg/kg)	Uncertainty[a] (mg/kg)	MRL[b] (mg/kg)
S3 (Grape)	Acetamiprid	0.181	0.009	0.35
	Cyprodinil	1.83	0.09	3
	Metrafenone	1.10	0.05	7
S4 (Coriander)	Fipronil	0.0835	0.0042	-[d]
	Iprodione	0.0706	0.0035	0.1
	Linuron	1.10	0.06	T2[e]

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

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

[c] Sum of indoxacarb and its R-isomer.

[d] Sum of fipronil, the sulphenyl metabolite (5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl) sulphenyl]-1H-pyrazole-3-carbonitrile), the sulphonyl metabolite (5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)sulphonyl]-1H-pyrazole-3-carbonitrile), and the trifluoromethyl metabolite (5-amino-4-trifluoromethyl-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-1H-pyrazole-3-carbonitrile).

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

2.2 Study Timetable

The timetable of the study was:

Invitations sent 11/05/2023

Samples sent 5/06/2023

Results due 10/07/2023

Interim Report 13/07/2023

Preliminary Report 19/07/2023

2.3 Participation and Laboratory Code

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

2.4 Sample Preparation

Four test samples were prepared by adding pesticide standard solutions to pureed tomatoes (Sample S1), bok choy (Sample S2), grapes (Sample S3) and coriander (Sample S4). Additional sample preparation details are provided in Appendix 1.

2.5 Homogeneity and Stability of Test Materials

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

Reports in the Joint FAO/WHO Meeting on Pesticide Residues (JMPR) database,[6] together with results of previous NMI PT studies of similar analytes and matrices, gave some assurance that the analytes selected were stable in frozen fresh produce. To further assess possible instability, the results returned by participants were compared to the spiked values (where applicable). For scored analytes, assigned values were between 81% and 102% of the spiked values. These values are similar to values observed in previous studies, and give good support for the stability of the samples. Actual transportation stability was also considered by

comparing participants' results to the number of days the samples spent in transit, and there was no evidence of analyte instability.

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

2.6 Sample Storage and Dispatch

After preparation, the samples were stored in a freezer at approximately -20 °C. Participants were sent 100 g portions of both spiked and unspiked Samples S1, S2 and S3, and 50 g portions of both spiked and unspiked Sample S4. The samples were packaged into insulated polystyrene foam boxes with cooler bricks and dispatched by courier on 5 June 2023.

The following items were also sent to participants:

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

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

2.7 Instructions to Participants

Participants were instructed as follows:

- Quantitatively analyse the samples using your routine test method.
- The unspiked material need not be analysed, it is provided for participants to use if they wish.
- Participants need not test for all analytes listed.
- Please thaw and thoroughly mix the PT samples before analysis.
- For each analyte in each sample report a single result on as received basis in units of mg/kg expressed as if reporting to a client (i.e. corrected for recovery or not, according to your standard procedure). This figure will be used in all statistical analysis in the study report.
- For each analyte in each sample report the associated expanded measurement uncertainty (e.g. 0.50 ± 0.02 mg/kg), if determined.
- Report any listed pesticide not tested as NT.
- Do not correct results for any pesticide found in the unspiked sample.
- No limit of reporting has been set for this study. Report results as you would to a client, applying the limit of reporting of the method used for analysis.
- Give details of your methodology and basis of uncertainty estimate as requested by the results sheet emailed to you.
- If determined, report your percentage recovery. This will be presented in the report for information only.
- Return the completed results sheet by 3 July 2023 by email to proficiency@measurement.gov.au.

The results due date was later extended to 10 July 2023 due to sample delivery delays to some international participants.

2.8 Interim Report and Preliminary Report

An Interim Report was emailed to all participants on 13 July 2023.

A Preliminary Report was emailed to all participants on 19 July 2023. This report included a summary of the results reported by participants, assigned values, performance coefficient of variations, *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.

3.2 Basis of Participants' Measurement Uncertainty Estimates

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

Table 3 Basis of MU Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
		Precision	Method Bias	
1	Horwitz formula	Control samples - SS Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS Standard purity	NMI Uncertainty Course
2	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS Standard purity	SANTE 12682/2019
3	Top Down - precision and estimates of the method and laboratory bias	Control samples Duplicate analysis Instrument calibration	Recoveries of SS	Eurachem/CITAC Guide
4	Standard deviation of replicate analyses multiplied by 2 or 3		Instrument calibration Recoveries of SS Standard purity	Eurachem/CITAC Guide
5	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis Instrument calibration	Instrument calibration Laboratory bias from PT studies Standard purity	SANTE 12682/2019
6	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis	Standard purity	Eurachem/CITAC Guide
7	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Instrument calibration	Instrument calibration Recoveries of SS	ISO/GUM
8	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM Duplicate analysis Instrument calibration	Recoveries of SS	Eurachem/CITAC Guide
9	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS		NATA Technical Note 33
10	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide
11		Control samples - SS	Recoveries of SS	
12	Top Down - precision and estimates of the method and laboratory bias	Control samples	CRM Recoveries of SS Standard purity	ISO/GUM

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
		Precision	Method Bias	
13	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples - SS Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	Nordtest Report TR537
14	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Instrument calibration Recoveries of SS Standard purity	Eurachem/CITAC Guide
15	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	SANCO12571/ 2013
16	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis	Instrument calibration Recoveries of SS	SANTE 12682/2019
17		Duplicate analysis	Recoveries of SS	
18	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Laboratory bias from PT studies Recoveries of SS	SANTE 12682/2019
19	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS Standard purity	Eurachem/CITAC Guide
20	Top Down - reproducibility (standard deviation) from PT studies used directly	Control samples - SS Duplicate analysis	Recoveries of SS	SANTE 12682/2019
21	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS Standard purity	Codex CAC/GL 59-2006 "Guidelines on Estimation of Uncertainty of Results" Annex 5.4

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

3.3 Participants' Comments

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

Table 4 Participants' Comments

Lab. Code	Sample	Participant's Comments	Study Coordinator's Response
1	S1	Fenhexamid and Chlorpyrifos methodology: average results	
	S2	Indoxacarb and Iprodione methodology: average results	
	S3	Prothiofos also detected at 0.0033 +/- 0.009, recovery 93 in S3. Chlorpyrifos, Fenhexamid, Bifenthrin, Pyrimethanil, Metalaxyl, Clothianidin, Methomyl, Prothiofos & Pyraclostrobin are present	

Lab. Code	Sample	Participant's Comments	Study Coordinator's Response
		in BLKS3 at a similar level to S3. Cyprodinil is in BLKS3 at a level of around 0.09. Chlorpyrifos, Cyprodinil, Fenhexamid, Metalaxyl and Metrafenone methodology: average results	
	S4	Note Chlorpyifos, Cypermethrin (possibly alpha Cypermethrin), Permethrin, Cyprodinil, Azoxystrobin, Imidacloprid & Fludioxonil are all present at similar levels in BLK S4 Chlorpyrifos and Cyprodinil methodology: average results	
2	S1, S2, S3	The concentration of residue reported is an average of four determinations made on the same sample. The unspiked sample was also analyzed and found to have no residues at or above the Limit of Quantitation (LOQ) at 0.01 mg/Kg. 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%	
	S1	Chlorpyrifos and Endosulfan sulfate methodology: Confirmatory analysis using GC-MS	
	S2	Bifenthrin and Iprodione methodology: Confirmatory analysis using GC-MS	
	S3	Bifenthrin methodology: Confirmatory analysis using GC-MS	
	S4	The detection of Fenvalerate and Permethrin was observed in all US4 trials. The results of Fenvalerate and Permethrin were calculated without recovery correction. The measurement units (MU) of Fenvalerate and Permethrin were obtained from the validation data. Fipronil and Permethrin methodology: Confirmatory analysis using GC-MS	
	All	This PT is important for the reliability and assessment of our laboratory's results, and also for compliance in accreditation. We would like to suggest PT studies for pesticide residues in other sample matrices such as rice, banana, pineapple, and mango. Uncertainty: The reported uncertainty of result is an expanded uncertainty calculated using a coverage factor of 2 which gives a level of confidence of approximately 95%.	Thank you for your feedback, we will take into consideration your suggestions for matrices when planning future studies.
4	S3	Found the following residue in the Unspiked samples: Methomyl, Metalaxyl, Fenhexamid,Fludioxinil, Cyprodinil, Prothiofos, Bifenthrin and Chlorpyrifos	
	S4	Found residue in the Unspike sample: Cyprodinil, Chlorpyrifos, Permethrin	
5	S3	S3 has incurred residues for the following compounds: Bifenthrin, Chlorpyrifos, Cyprodinil, Fenhexamid, Fludioxonil, Metalaxyl	
	S4	S4 has incurred residues for the following compounds: Chlorpyrifos, Imidacloprid and Permethrin	
6	S3	Blank Grapes Contains following compounds (1) Bifenthrin 0.029 mg/kg (2) Chlorpyrifos 0.038 mg/kg (3) Cyprodinil 0.08 mg/kg (4) Fludioxonil 0.025mg/kg (5) Metalaxyl 0.054 mg/kg (6) Prothiofos 0.036 mg/kg (7) Pyraclostobin 0.005 mg/kg -- <LOR 0.01 (8) Pyrimethanil 0.007 mg/kg -- <LOR 0.01 (9) Fenhexamid 0.022 mg /kg (10) Methomyl 0.035 mg/kg.	

Lab. Code	Sample	Participant's Comments	Study Coordinator's Response
	S4	Blank coriander detected following compounds (1) Chlorpyrifos 0.018 mg/kg (2) Cypermethrin 0.016mg/kg (3) Cyprodinil 0.026 mg/kg (4) Fludioxonil 0.006 mg/kg -- <LOR 0.01 (5) Myclobutanil 0.008 mg/kg -- <LOR 0.01 (6) Permethrin 0.166 mg/kg (7) Azoxystrobin 0.012 mg/kg.	
7	S2	Sample and blank contained trace levels of 2-Aminobenzimidazole.	
	S3	Sample contained reportable levels of prothiofos (0.03mg/kg) and pyrimethanil (0.01mg/kg). Sample contained trace level of clothianidin, ethy-spinosyn J, pyraclostrobin. Blank sample contains bifenthrin (0.02mg/kg), chlorpyrifos (0.04mg/kg), cyprodonil (0.07mg/kg), fenhexamid (0.03mg/kg), fludioxonil (0.02mg/kg), metalaxyl (0.07mg/kg), methomyl (0.03mg/kg), prothiofos (0.03mg/kg). Blank sample contains trace levels of clothianidin, ehtyl-spinoyn J, pyraclostrobin.	
	S4	Sample contains trace levels of azoxystrobin, fludioxonil, imidacloprid, metolachlor. Blank sample contains trace levels of azoxystrobin, fludioxonil, linuron, metolachlor. Blank sample contains cypermethrin (0.21mg/kg), chlorpyrifos (0.01mg/kg), cyprodonil (0.02mg/kg), permethrin (0.17mg/kg).	
	All	A lot of incurred residues in some samples - not sure if intended or not, but will be interesting to see in final report. Reporting of results has become very dated - same sheet in use for 15+ years - time to look at an online portal, or more user friendly table. Indication of methodologies used for every compound, in every sample is a waste of time. Brief overview sufficient.	Thank you for your feedback. We have recently added the template for completing methodology tables. We will investigate other ways to make the tables more user friendly. Unfortunately, we are currently unable to offer an online portal for submission of results.
9	S3	Unspiked grape sample were detected for Bifenthrin - 0.017mg/kg, Chlopyrifos -0.024 mg/kg, Cyprodinil - 0.113 mg/kg, Fenhaxamid - 0.035 mg/kg, Fludioxonil - 0.024 mg/kg, Metalaxyl - 0.043 mg/kg and Methomyl - 0.037 mg/kg.	
	S4	Unspiked corriander sample was detected for Chlopyrifos-0.015 mg/kg, Cyprodinil - 0.017 mg/kg, Cypermethrin 0.134 mg/kg, Permethrin 0.16mg/kg.	
10	S3, S4	Found Chlorpyrifos in unspiked sample	
12	S3	Positives for bifenthrin, chlorpyrifos, fenhexamid, metalaxyl, methomyl and prothiofos also present at the same levels in unspiked sample. Postive of 0.06 mg/kg detected for cyprodinil in the unspiked sample.	
	S4	Chlorpyrifos and cyprodinil positives in unspiked sample at the same level as above.	
15	S3	Prothiofos 0.024 mg/kg. Blank is positive for: Bifenthrin, Chlorpyrifos, Clothianidin, Cyprodinil, Fenhexamid, Fludioxonil, Metalaxyl, Methomyl	

Lab. Code	Sample	Participant's Comments	Study Coordinator's Response
16	S1	Endosulfan sulfate is corrected	
	S2	results are corrected	
	S3	detection in control: 0.02 chlorpyrifos ; 0.0 bifenthrin	
	S4	results are not corrected	
19	S1	Chlorpyrifos and Endosulfan sulfate methodology: EN 15662:2018	
	S2	Bifenthrin methodology: EN 15662:2018	
	S3	Bifenthrin, Chlorpyrifos and Metalaxyl methodology: EN 15662:2018	
	S4	Chlorpyrifos, Cypermethrin, Fipronil and Permethrin methodology: EN 15662:2018	
	All	<LOQ means less than 0.01ppm or no detection at all. Recovery correction was accounted in reporting the final concentrations.	

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 5 to 26 with summary statistics: robust average, median, mean, number of numeric results (N), maximum (Max), minimum (Min), robust standard deviation (Robust SD) and robust coefficient of variation (Robust CV). Bar charts of results and performance scores are presented in Figures 2 to 23. An example chart with interpretation guide is shown in Figure 1.

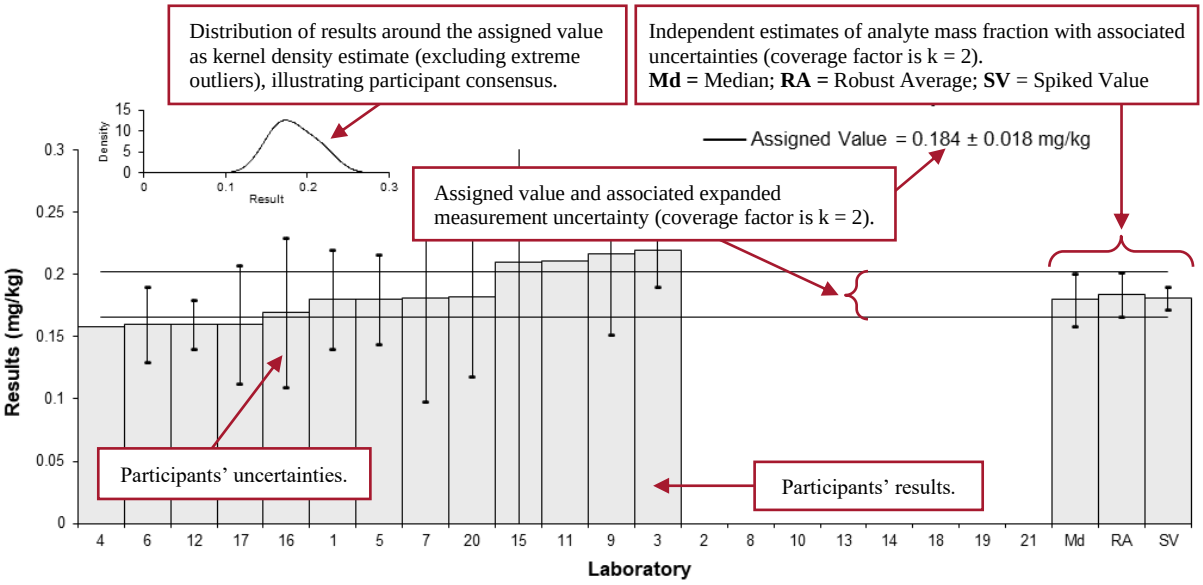


Figure 1 Guide to Presentation of Results

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 of a proficiency test item'.[1] In this PT study, this property is the mass fraction of the analytes in the samples. The assigned values for all scored analytes were the robust averages of participants' results, and the expanded uncertainties were estimated from the associated robust SDs (Appendix 3).

4.4 Robust Average and Robust Between-Laboratory Coefficient of Variation

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

4.5 Performance Coefficient of Variation

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

4.6 Target Standard Deviation for Proficiency Assessment

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

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

4.7 *z*-Score

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

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

where:

z is *z*-score

χ is a participant's result

X is the assigned value

σ is the target standard deviation for proficiency assessment from Equation 1

For the absolute value of a *z*-score:

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

4.8 E_n-Score

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

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

where:

E_n is E_n-score

χ is a participant's result

X is the assigned value

U_χ is the expanded measurement uncertainty of the participant's result

U_X is the expanded measurement uncertainty of the assigned value

For the absolute value of an E_n-score:

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

4.9 Traceability and Measurement Uncertainty

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

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

5 TABLES AND FIGURES

Table 5

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	0.59	0.1	96
2	NT	NT	NT
3	0.18	0.03	69
4	0.43	0.184	64
5	0.51	0.1	NR
6	0.41	0.19	69
7	0.331	0.0993	NR
8	NT	NT	NT
9	0.312	0.094	100
10	0.35	NR	104
11	NT	NT	NT
12	0.51	0.077	88.67
13	0.419	0.0229	88.5
14	0.176	NR	101.44
15	NT	NT	NT
16	NR	NR	NR
17	0.27	0.081	75
18	NT	NT	NT
19	NT	NT	NT
20	NT	NT	NT
21	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	0.998	0.050
Robust Average	0.37	0.11
Median	0.380	0.095
Mean	0.374	
N	12	
Max	0.59	
Min	0.176	
Robust SD	0.15	
Robust CV	39%	

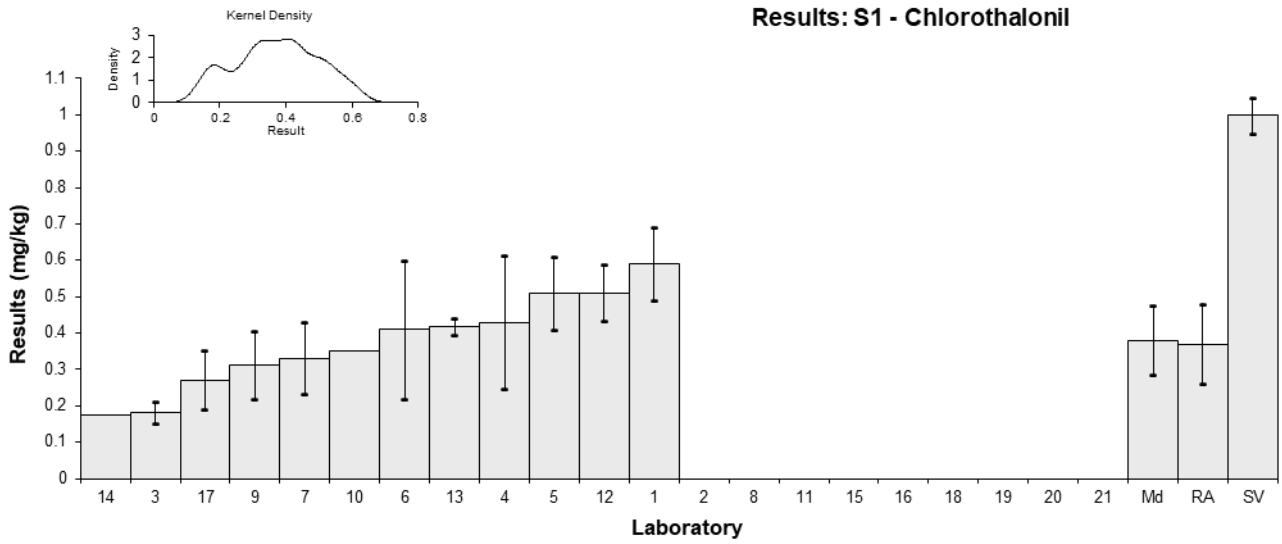

Results: S1 - Chlorothalonil
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
14 3 17 9 7 10 6 13 4 5 12 1 2 8 11 15 16 18 19 20 21 Md RA SV

Figure 2

Table 6

Sample Details

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

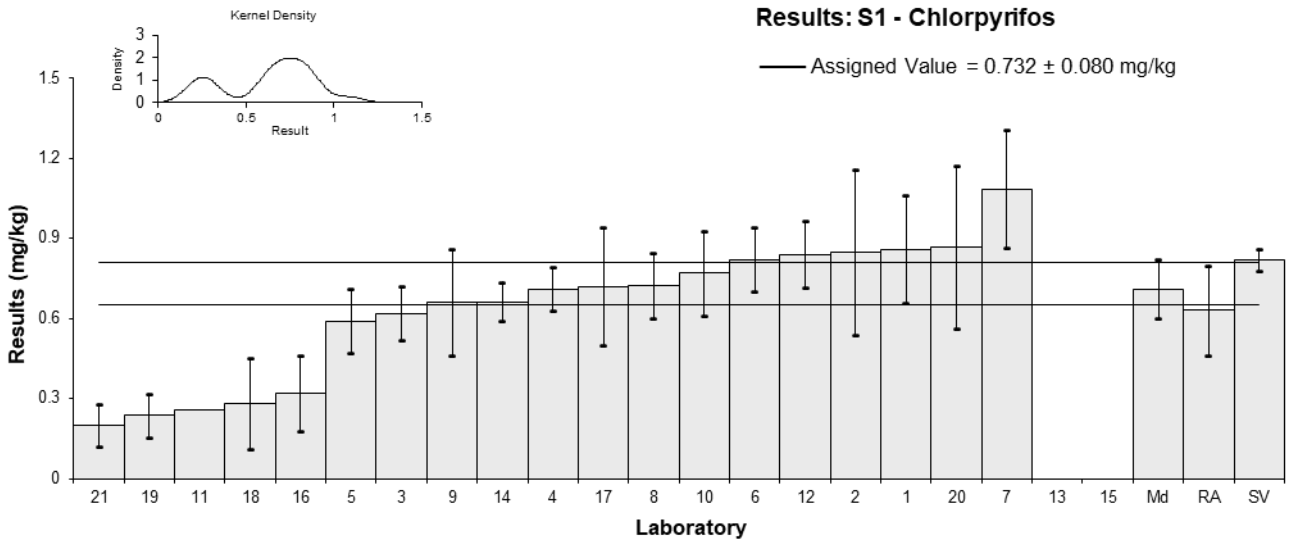
Participant Results

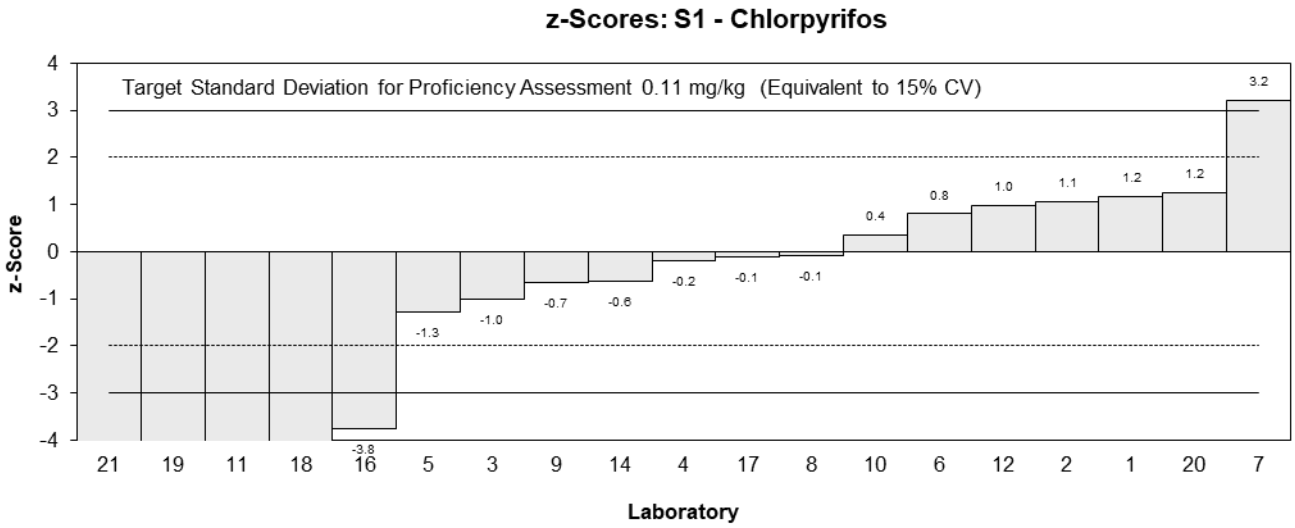
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.86	0.2	98	1.17	0.59
2	0.85	0.31	95.72	1.07	0.37
3	0.62	0.1	90	-1.02	-0.87
4	0.71	0.082	97	-0.20	-0.19
5	0.59	0.12	NR	-1.29	-0.98
6	0.82	0.12	86	0.80	0.61
7*	1.086	0.221	NR	3.22	1.51
8	0.723	0.1227	116	-0.08	-0.06
9	0.66	0.20	100	-0.66	-0.33
10	0.77	0.16	87	0.35	0.21
11*	0.255	NR	80	-4.34	-5.96
12	0.84	0.126	83.98	0.98	0.72
13	NT	NT	NT		
14	0.663	0.073	113.93	-0.63	-0.64
15	NT	NT	NT		
16	0.32	0.14	105	-3.75	-2.56
17	0.72	0.22	68	-0.11	-0.05
18*	0.28	0.17	98	-4.12	-2.41
19*	0.237	0.081	57	-4.51	-4.35
20	0.868	0.304	90	1.24	0.43
21*	0.20	0.08	154	-4.85	-4.70

* Outlier, see Section 4.2

Statistics

Assigned Value	0.732	0.080
Spike Value	0.821	0.041
Robust Average	0.63	0.17
Median	0.71	0.11
Mean	0.64	
N	19	
Max	1.086	
Min	0.2	
Robust SD	0.29	
Robust CV	46%	


Kernel Density
Density
Result
Results: S1 - Chlorpyrifos
Assigned Value = 0.732 ± 0.080 mg/kg
Results (mg/kg)
Laboratory
21 19 11 18 16 5 3 9 14 4 17 8 10 6 12 2 1 20 7 13 15 Md RA SV


z-Scores: S1 - Chlorpyrifos
Target Standard Deviation for Proficiency Assessment 0.11 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
21 19 11 18 16 5 3 9 14 4 17 8 10 6 12 2 1 20 7
-3.8 -1.3 -1.0 -0.7 -0.6 -0.2 -0.1 -0.1 0.4 0.8 1.0 1.1 1.2 1.2 3.2

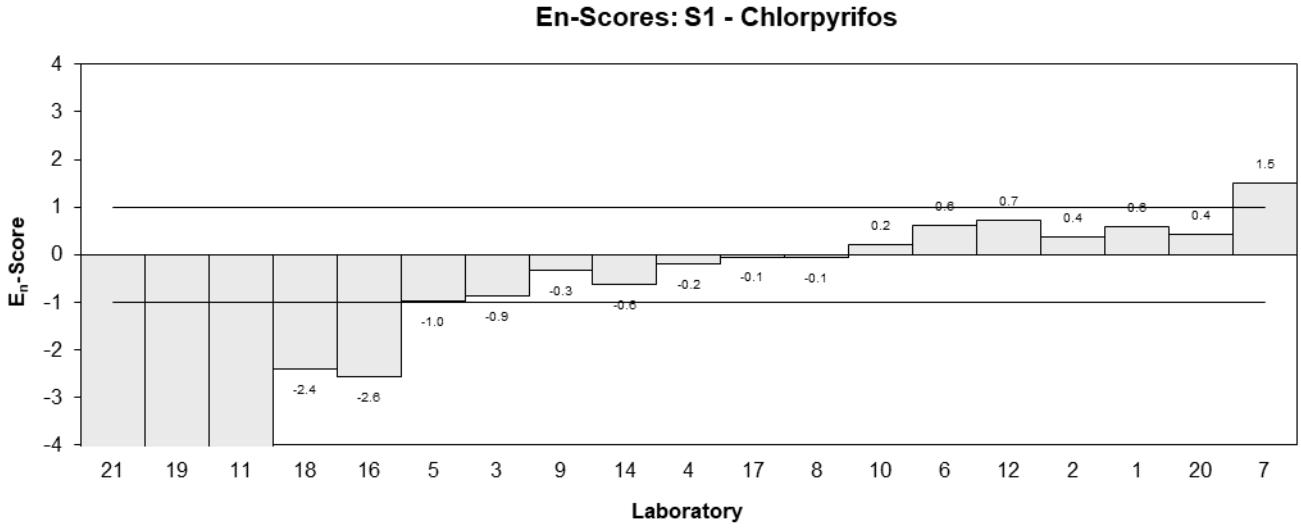

En-Scores: S1 - Chlorpyrifos
En-Score
Laboratory
21 19 11 18 16 5 3 9 14 4 17 8 10 6 12 2 1 20 7
-2.4 -2.6 -1.0 -0.9 -0.3 -0.6 -0.2 -0.1 -0.1 0.2 0.6 0.7 0.4 0.6 0.4 1.5

Figure 3

Table 7

Sample Details

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

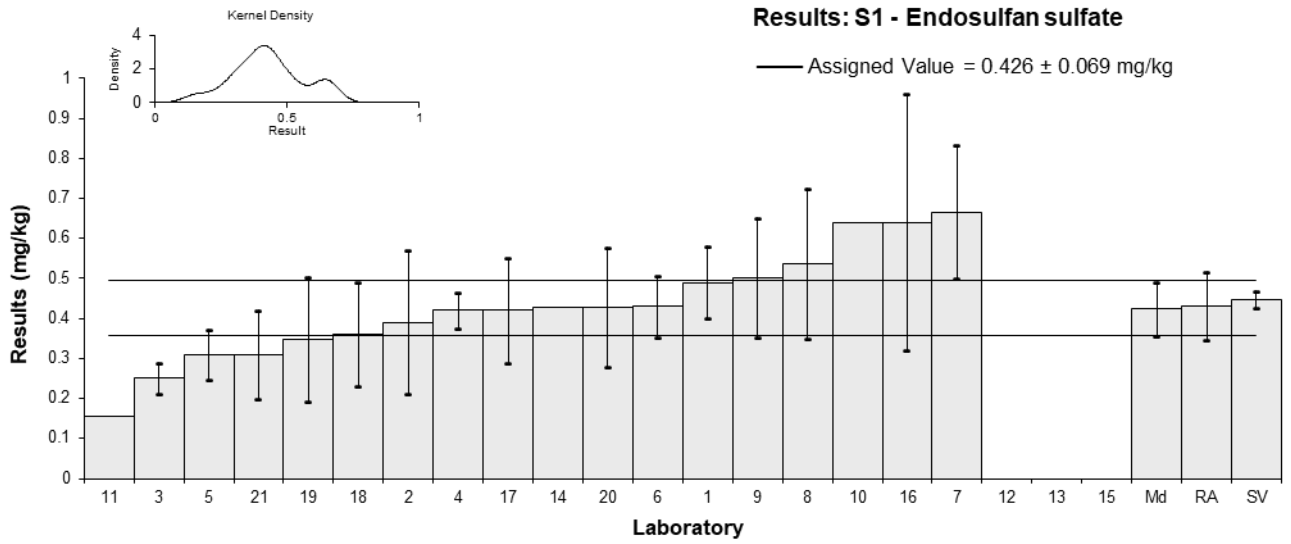
Participant Results

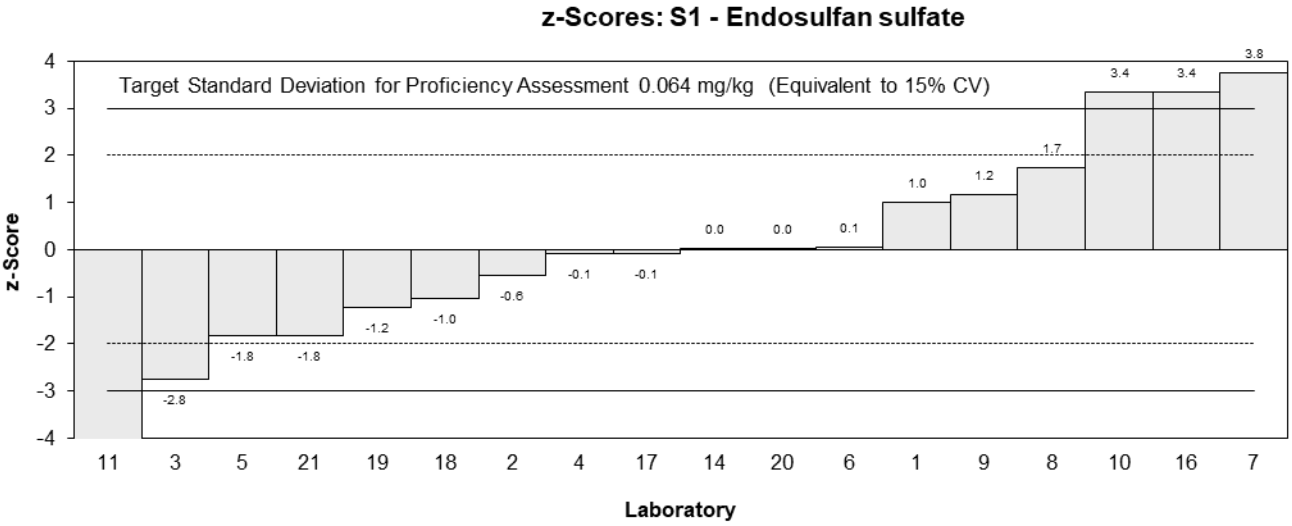
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.49	0.09	97	1.00	0.56
2	0.39	0.18	78.16	-0.56	-0.19
3	0.25	0.04	87	-2.75	-2.21
4	0.42	0.044	69	-0.09	-0.07
5	0.31	0.062	NR	-1.82	-1.25
6	0.43	0.076	106	0.06	0.04
7*	0.666	0.1665	NR	3.76	1.33
8	0.537	0.188	147	1.74	0.55
9	0.501	0.150	102	1.17	0.45
10	0.64	NR	122	3.35	3.10
11*	0.156	NR	107	-4.23	-3.91
12	NT	NT	NT		
13	NT	NT	NT		
14	0.428	NR	119.25	0.03	0.03
15	NT	NT	NT		
16	0.64	0.32	74	3.35	0.65
17	0.42	0.13	81	-0.09	-0.04
18	0.36	0.13	118	-1.03	-0.45
19	0.348	0.156	107	-1.22	-0.46
20	0.428	0.150	100	0.03	0.01
21	0.31	0.11	76	-1.82	-0.89

* Outlier, see Section 4.2

Statistics

Assigned Value	0.426	0.069
Spike Value	0.447	0.022
Robust Average	0.431	0.085
Median	0.424	0.067
Mean	0.429	
N	18	
Max	0.666	
Min	0.156	
Robust SD	0.14	
Robust CV	34%	


Kernel Density
Density
Result
Results: S1 - Endosulfan sulfate
Assigned Value = 0.426 ± 0.069 mg/kg
Results (mg/kg)
Laboratory
11 3 5 21 19 18 2 4 17 14 20 6 1 9 8 10 16 7 12 13 15 Md RA SV


z-Scores: S1 - Endosulfan sulfate
Target Standard Deviation for Proficiency Assessment 0.064 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
11 3 5 21 19 18 2 4 17 14 20 6 1 9 8 10 16 7
-2.8 -1.8 -1.8 -1.2 -1.0 -0.6 -0.1 -0.1 0.0 0.0 0.1 1.0 1.2 1.7 3.4 3.4 3.8

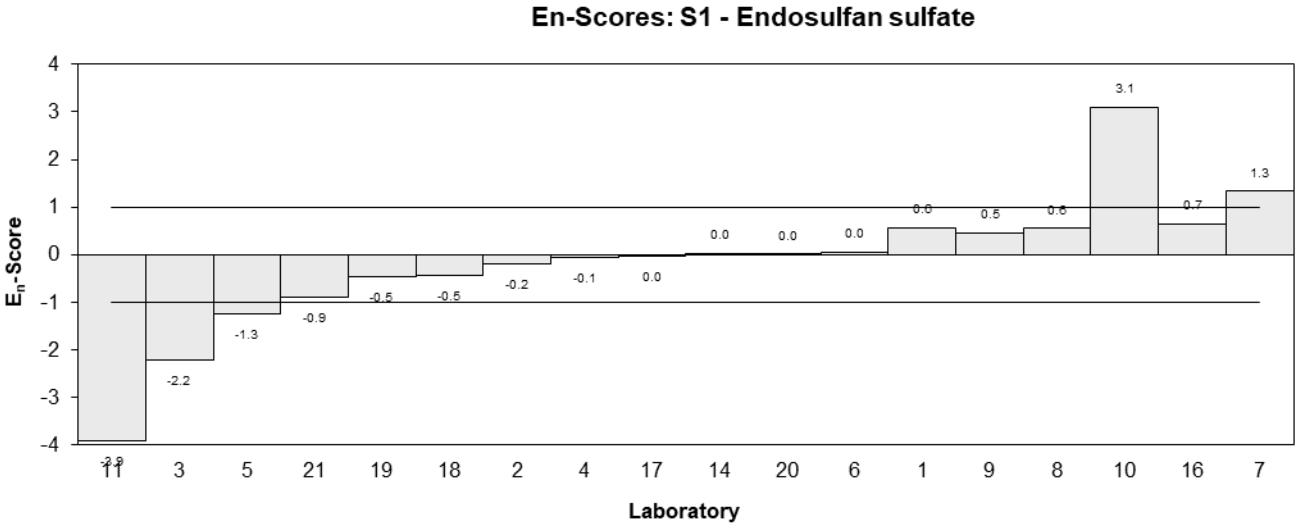

En-Scores: S1 - Endosulfan sulfate
En-Score
Laboratory
11 3 5 21 19 18 2 4 17 14 20 6 1 9 8 10 16 7
-2.2 -1.3 -0.9 -0.5 -0.5 -0.2 -0.1 0.0 0.0 0.0 0.0 0.5 0.6 3.1 0.7 1.3

Figure 4

Table 8

Sample Details

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

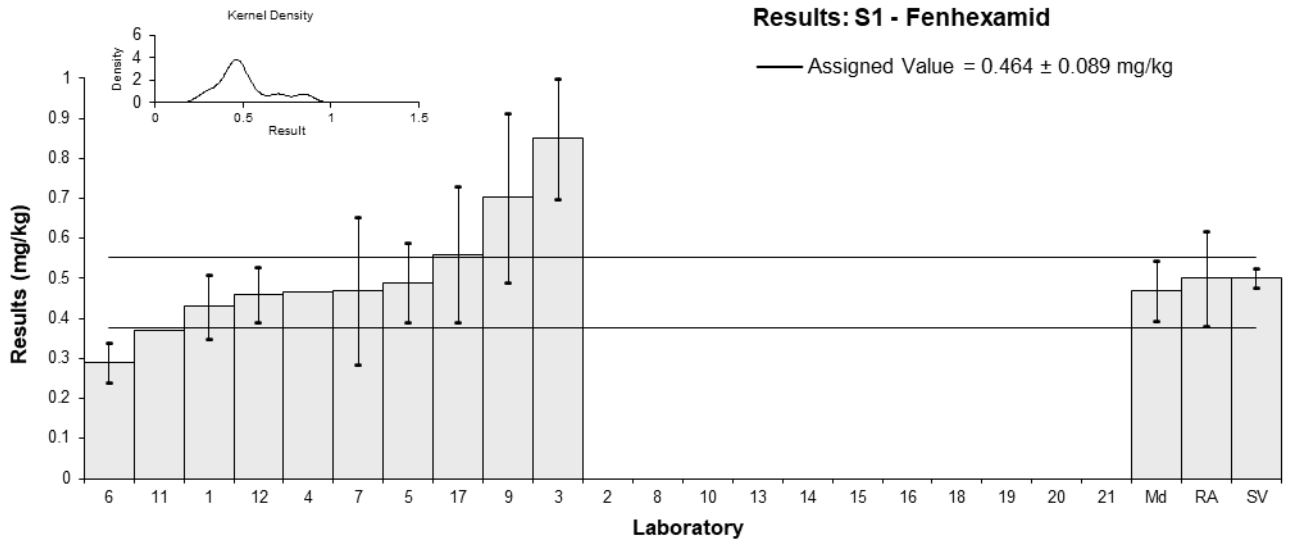
Participant Results

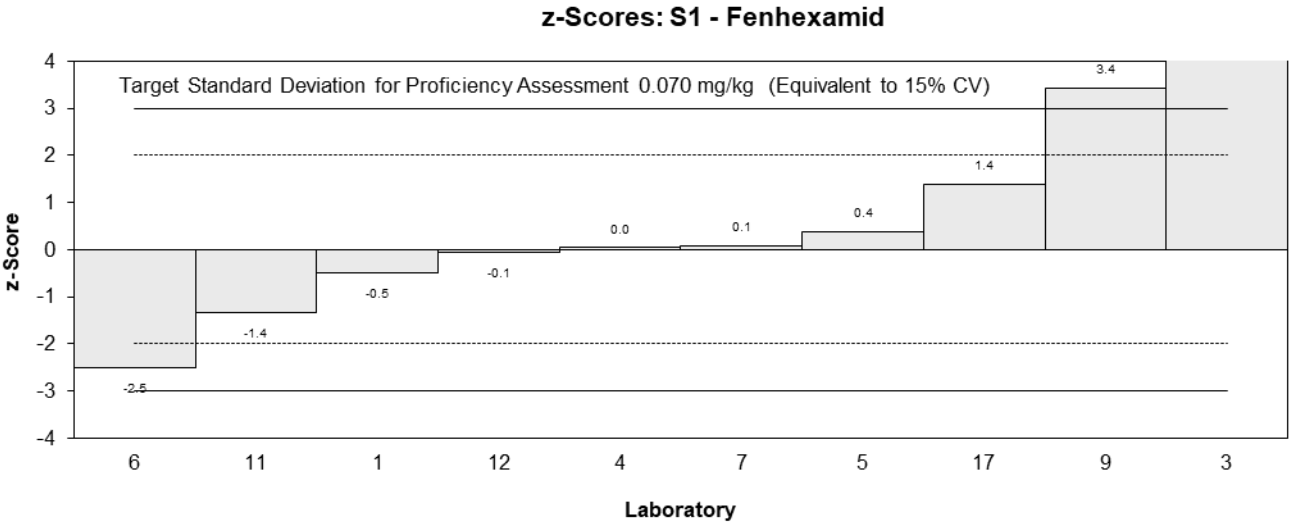
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.43	0.08	98	-0.49	-0.28
2	NT	NT	NT		
3*	0.85	0.15	75	5.55	2.21
4	0.467	NR	96	0.04	0.03
5	0.49	0.098	NR	0.37	0.20
6	0.29	0.05	117	-2.50	-1.70
7	0.4701	0.184	NR	0.09	0.03
8	NT	NT	NT		
9	0.702	0.211	71	3.42	1.04
10	NT	NT	NT		
11	0.370	NR	71	-1.35	-1.06
12	0.46	0.07	88.44	-0.06	-0.04
13	NT	NT	NT		
14	NT	NT	NT		
15	NT	NT	NT		
16	NT	NT	NT		
17	0.56	0.17	97	1.38	0.50
18	NT	NT	NT		
19	NT	NT	NT		
20	NT	NT	NT		
21	NT	NT	NT		

* Outlier, see Section 4.2

Statistics

Assigned Value	0.464	0.089
Spike Value	0.502	0.025
Robust Average	0.50	0.12
Median	0.469	0.076
Mean	0.51	
N	10	
Max	0.85	
Min	0.29	
Robust SD	0.15	
Robust CV	31%	


Kernel Density
Density
Result
Results: S1 - Fenhexamid
Assigned Value = 0.464 ± 0.089 mg/kg
Results (mg/kg)
Laboratory
6 11 1 12 4 7 5 17 9 3 2 8 10 13 14 15 16 18 19 20 21 Md RA SV


z-Scores: S1 - Fenhexamid
Target Standard Deviation for Proficiency Assessment 0.070 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
6 11 1 12 4 7 5 17 9 3
-2.5
-1.4
-0.5
-0.1
0.0
0.1
0.4
1.4
3.4

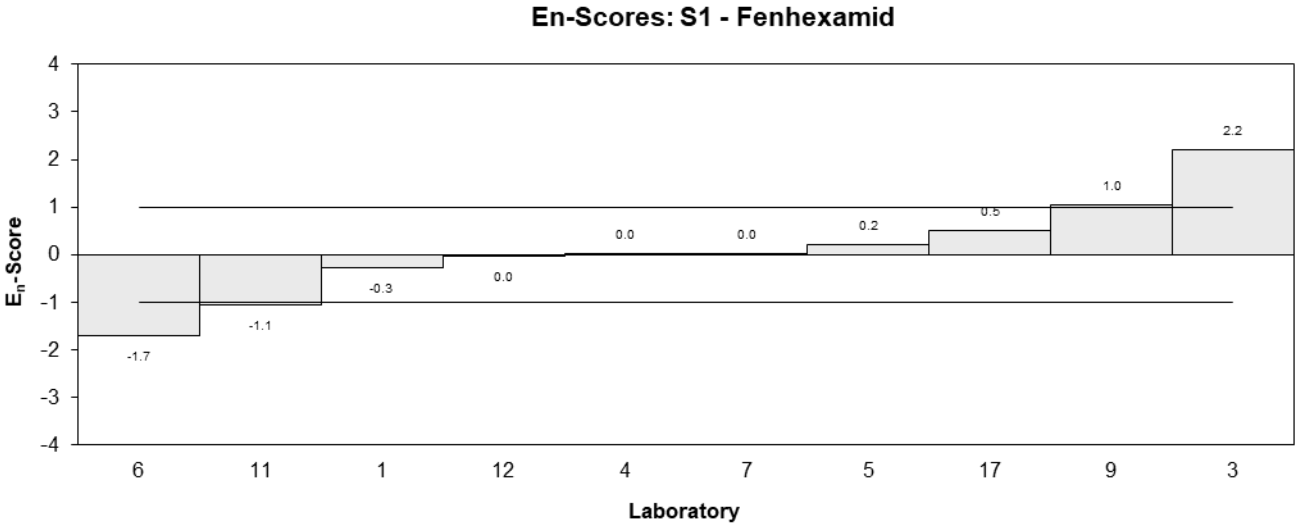

En-Scores: S1 - Fenhexamid
En-Score
Laboratory
6 11 1 12 4 7 5 17 9 3
-1.7
-1.1
-0.3
0.0
0.0
0.0
0.2
0.5
1.0
2.2

Figure 5

Table 9

Sample Details

Sample No.	S2
Matrix	Bok Choy
Analyte	Bifenthrin
Unit	mg/kg

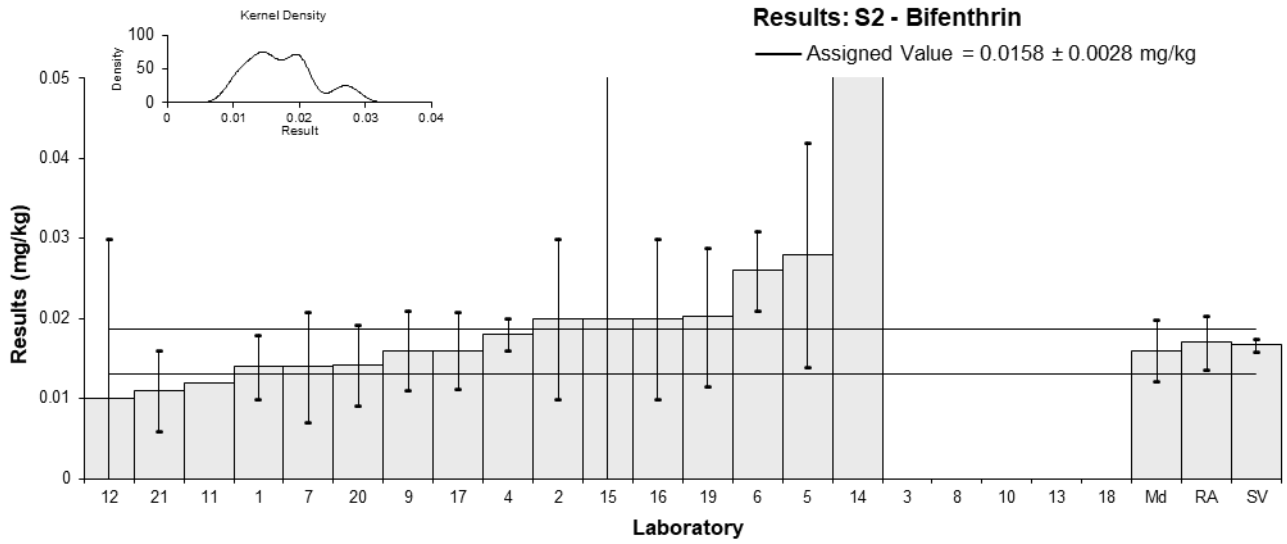
Participant Results

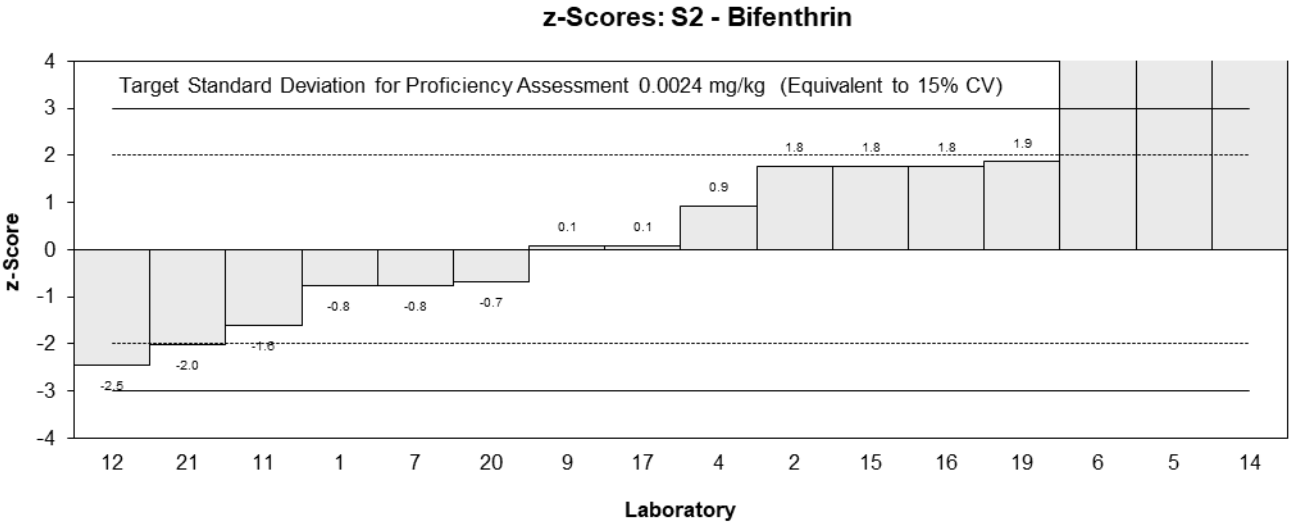
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.014	0.004	98	-0.76	-0.37
2	0.02	0.01	91.03	1.77	0.40
3	NR	NR	NR		
4	0.018	0.002	97	0.93	0.64
5*	0.028	0.014	NR	5.15	0.85
6*	0.026	0.005	81	4.30	1.78
7	0.014	0.0069	NR	-0.76	-0.24
8	NT	NT	NT		
9	0.016	0.005	112	0.08	0.03
10	NR	NR	NR		
11	0.012	NR	95	-1.60	-1.36
12	0.01	0.02	99.71	-2.45	-0.29
13	NT	NT	NT		
14**	0.136	NR	105.43	50.72	42.93
15	0.02	50	99	1.77	0.00
16	0.02	0.01	NR	1.77	0.40
17	0.016	0.0048	62	0.08	0.04
18	<0.01	NR	95		
19	0.0202	0.0087	68	1.86	0.48
20	0.0142	0.0050	79	-0.68	-0.28
21	0.011	0.005	94	-2.03	-0.84

* Outlier, ** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.0158	0.0028
Spike Value	0.0167	0.0008
Robust Average	0.0170	0.0034
Median	0.0160	0.0038
Mean	0.0173	
N	15	
Max	0.028	
Min	0.01	
Robust SD	0.0053	
Robust CV	31%	


Kernel Density
Density
Result
Results: S2 - Bifenthrin
Assigned Value = 0.0158 ± 0.0028 mg/kg
Results (mg/kg)
Laboratory
12 21 11 1 7 20 9 17 4 2 15 16 19 6 5 14 3 8 10 13 18 Md RA SV


z-Scores: S2 - Bifenthrin
Target Standard Deviation for Proficiency Assessment 0.0024 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
12 21 11 1 7 20 9 17 4 2 15 16 19 6 5 14

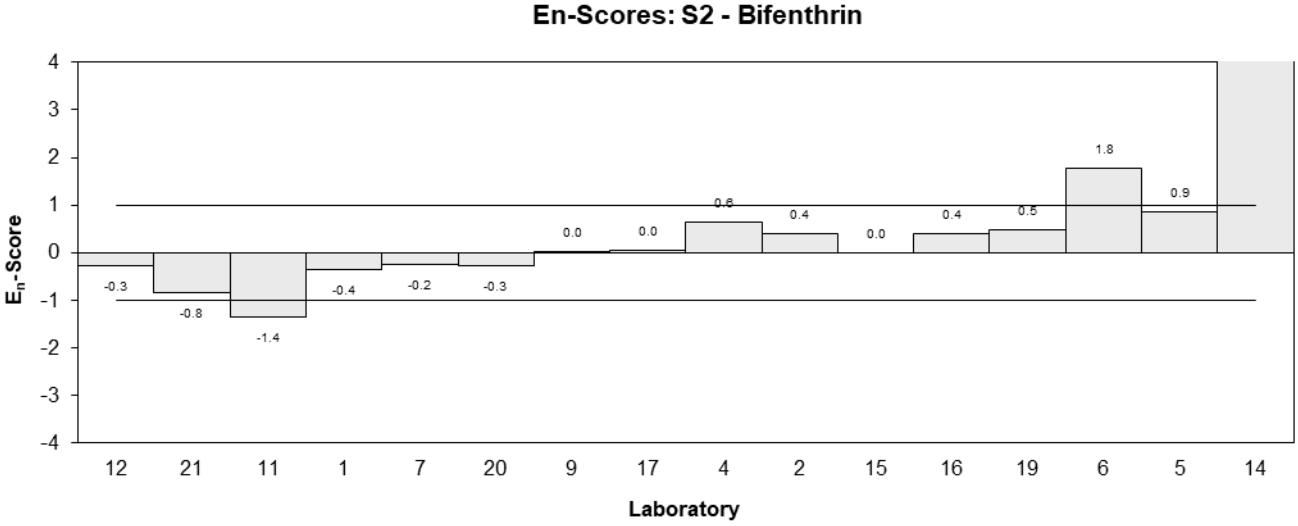

En-Scores: S2 - Bifenthrin
En-Score
Laboratory
12 21 11 1 7 20 9 17 4 2 15 16 19 6 5 14

Figure 6

Table 10

Sample Details

Sample No.	S2
Matrix	Bok Choy
Analyte	Indoxacarb
Unit	mg/kg

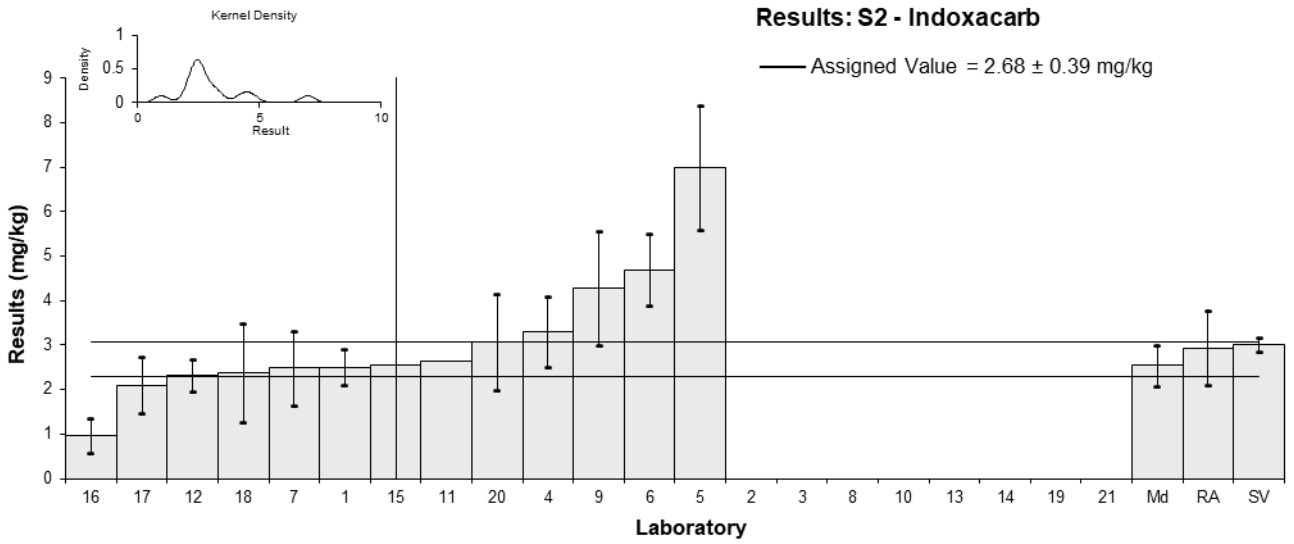
Participant Results

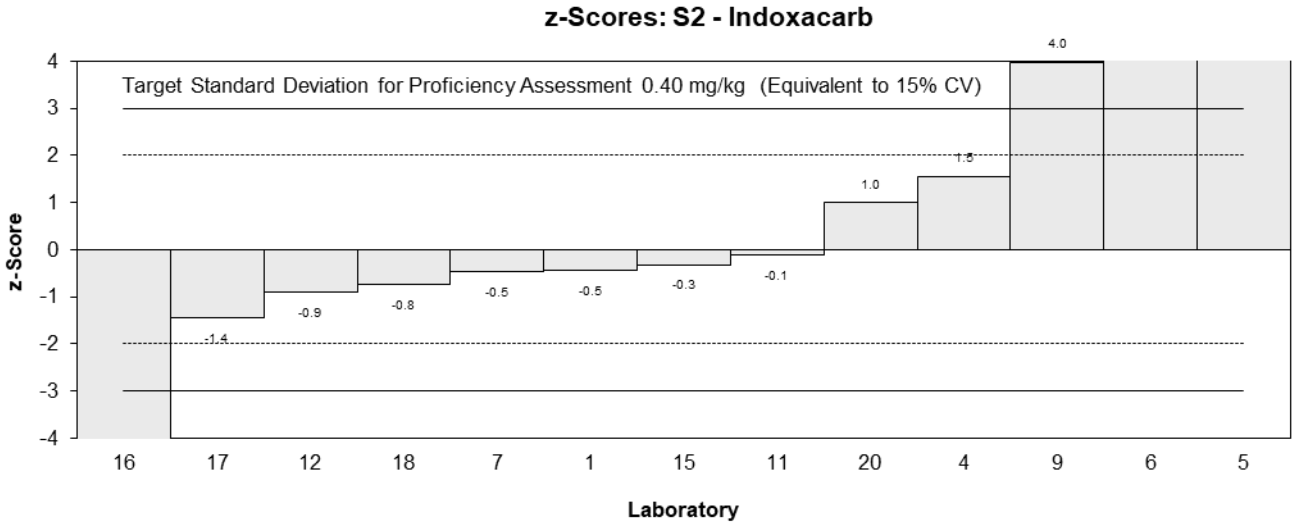
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	2.5	0.4	85	-0.45	-0.32
2	NT	NT	NT		
3	NT	NT	NT		
4	3.3	0.8	94	1.54	0.70
5*	7	1.4	NR	10.75	2.97
6*	4.70	0.80	115	5.02	2.27
7	2.4896	0.841	NR	-0.47	-0.21
8	NT	NT	NT		
9	4.28	1.28	86	3.98	1.20
10	NT	NT	NT		
11	2.630	NR	97	-0.12	-0.13
12	2.32	0.35	81.52	-0.90	-0.69
13	NT	NT	NT		
14	NT	NT	NT		
15	2.55	50	97	-0.32	0.00
16*	0.98	0.39	87	-4.23	-3.08
17	2.1	0.63	66	-1.44	-0.78
18	2.38	1.12	95	-0.75	-0.25
19	NT	NT	NT		
20	3.077	1.077	98	0.99	0.35
21	NT	NT	NT		

* Outlier, see Section 4.2

Statistics

Assigned Value	2.68	0.39
Spike Value	3.01	0.15
Robust Average	2.94	0.84
Median	2.55	0.46
Mean	3.10	
N	13	
Max	7	
Min	0.98	
Robust SD	1.2	
Robust CV	41%	


Kernel Density
Density
Result
Results: S2 - Indoxacarb
Assigned Value = 2.68 ± 0.39 mg/kg
Results (mg/kg)
Laboratory
16 17 12 18 7 1 15 11 20 4 9 6 5 2 3 8 10 13 14 19 21 Md RA SV


z-Scores: S2 - Indoxacarb
Target Standard Deviation for Proficiency Assessment 0.40 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
16 17 12 18 7 1 15 11 20 4 9 6 5
-1.4
-0.9
-0.8
-0.5
-0.5
-0.3
-0.1
1.0
1.5
4.0

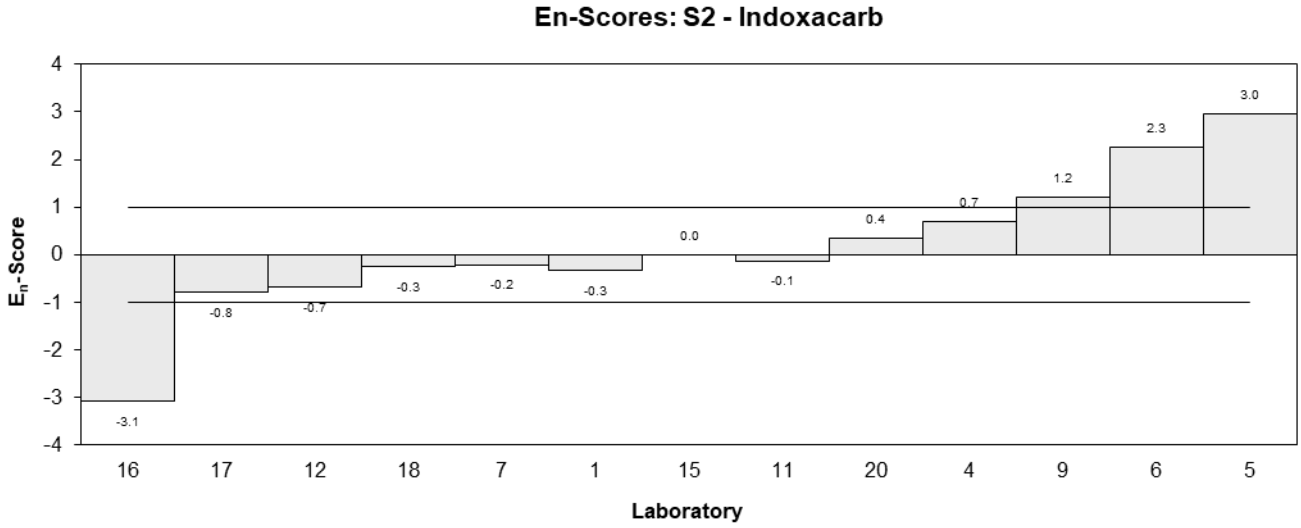

En-Scores: S2 - Indoxacarb
En-Score
Laboratory
16 17 12 18 7 1 15 11 20 4 9 6 5
-3.1
-0.8
-0.7
-0.3
-0.2
-0.3
0.0
-0.1
0.4
0.7
1.2
2.3
3.0

Figure 7

Table 11

Sample Details

Sample No.	S2
Matrix	Bok Choy
Analyte	Iprodione
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	6.8	0.8	93
2	4.58	2.19	106.42
3	3.1	0.5	93
4	5.3	1	88
5	11	2.2	NR
6	5.80	0.93	101
7	NT	NT	NT
8	NT	NT	NT
9	0.95	0.29	104
10	NT	NT	NT
11	<0.02	NR	NR
12	6.71	0.67	91.56
13	3.03	0.362	112.7
14	NT	NT	NT
15	8.15	50	90
16	1.4	0.56	91
17	5.5	1.7	80
18	7.41	3.43	75
19	NT	NT	NT
20	6.913	2.420	86
21	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	8.04	0.40
Robust Average	5.4	1.9
Median	5.7	1.5
Mean	5.5	
N	14	
Max	11	
Min	0.95	
Robust SD	2.8	
Robust CV	53%	

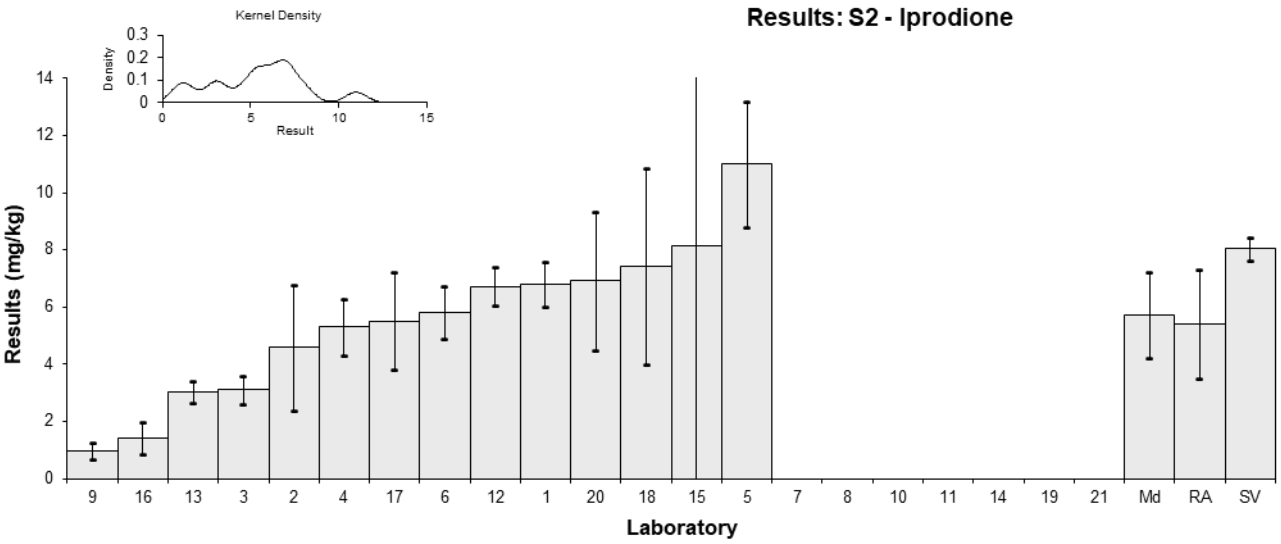

Results: S2 - Iprodione
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
9
16
13
3
2
4
17
6
12
1
20
18
15
5
7
8
10
11
14
19
21
Md
RA
SV

Figure 8

Table 12

Sample Details

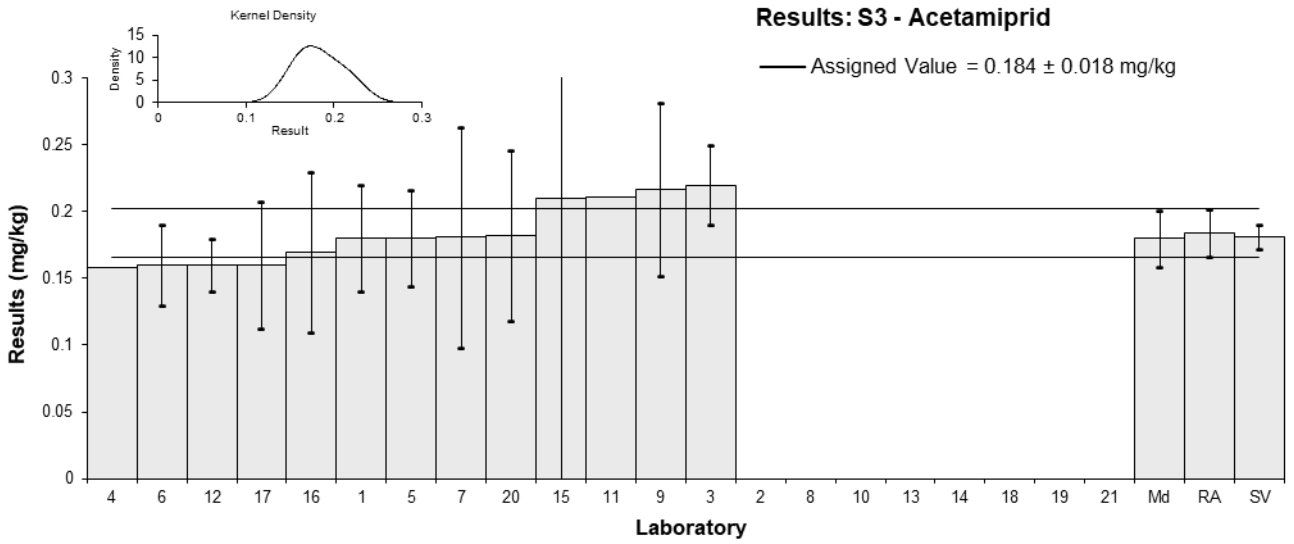
Sample No.	S3
Matrix	Grape
Analyte	Acetamiprid
Unit	mg/kg

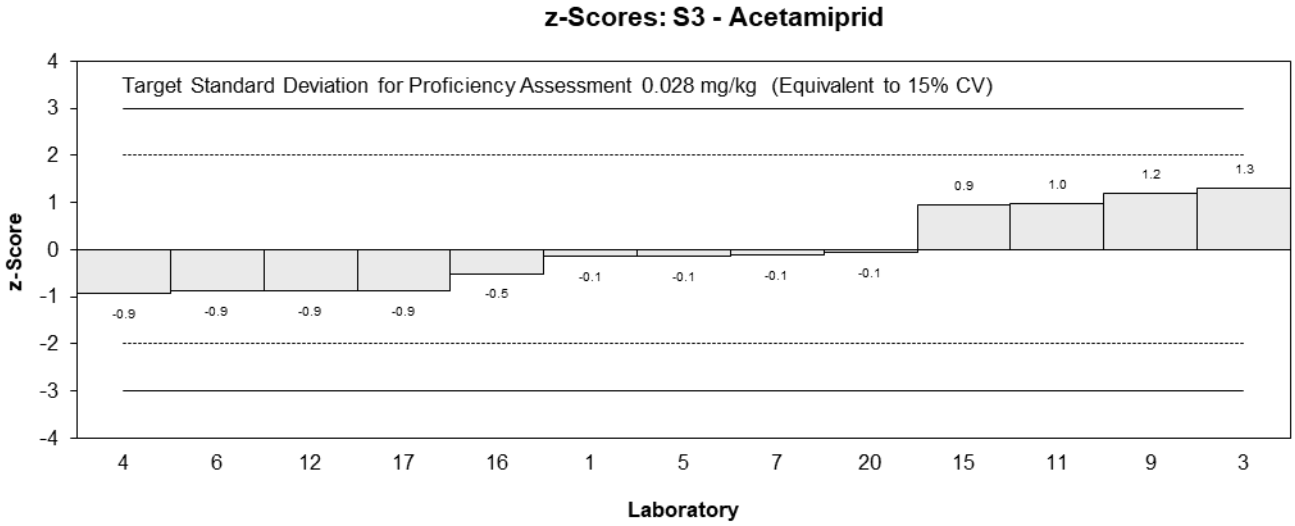
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.18	0.04	95	-0.14	-0.09
2	NT	NT	NT		
3	0.22	0.03	82	1.30	1.03
4	0.158	NR	90	-0.94	-1.44
5	0.18	0.036	NR	-0.14	-0.10
6	0.16	0.030	109	-0.87	-0.69
7	0.1808	0.083	NR	-0.12	-0.04
8	NT	NT	NT		
9	0.217	0.065	104	1.20	0.49
10	NT	NT	NT		
11	0.211	NR	69	0.98	1.50
12	0.16	0.02	99.48	-0.87	-0.89
13	NT	NT	NT		
14	NT	NT	NT		
15	0.21	50	146	0.94	0.00
16	0.17	0.06	NR	-0.51	-0.22
17	0.16	0.048	86	-0.87	-0.47
18	NT	NT	NT		
19	NT	NT	NT		
20	0.182	0.064	94	-0.07	-0.03
21	NT	NT	NT		

Statistics

Assigned Value	0.184	0.018
Spike Value	0.181	0.009
Robust Average	0.184	0.018
Median	0.180	0.021
Mean	0.184	
N	13	
Max	0.22	
Min	0.158	
Robust SD	0.026	
Robust CV	14%	


Kernel Density
Density
Result
Results: S3 - Acetamiprid
Assigned Value = 0.184 ± 0.018 mg/kg
Results (mg/kg)
Laboratory
4 6 12 17 16 1 5 7 20 15 11 9 3 2 8 10 13 14 18 19 21 Md RA SV


z-Scores: S3 - Acetamiprid
Target Standard Deviation for Proficiency Assessment 0.028 mg/kg (Equivalent to 15% CV)
z-Score
-0.9 -0.9 -0.9 -0.9 -0.5 -0.1 -0.1 -0.1 -0.1 0.9 1.0 1.2 1.3
Laboratory
4 6 12 17 16 1 5 7 20 15 11 9 3

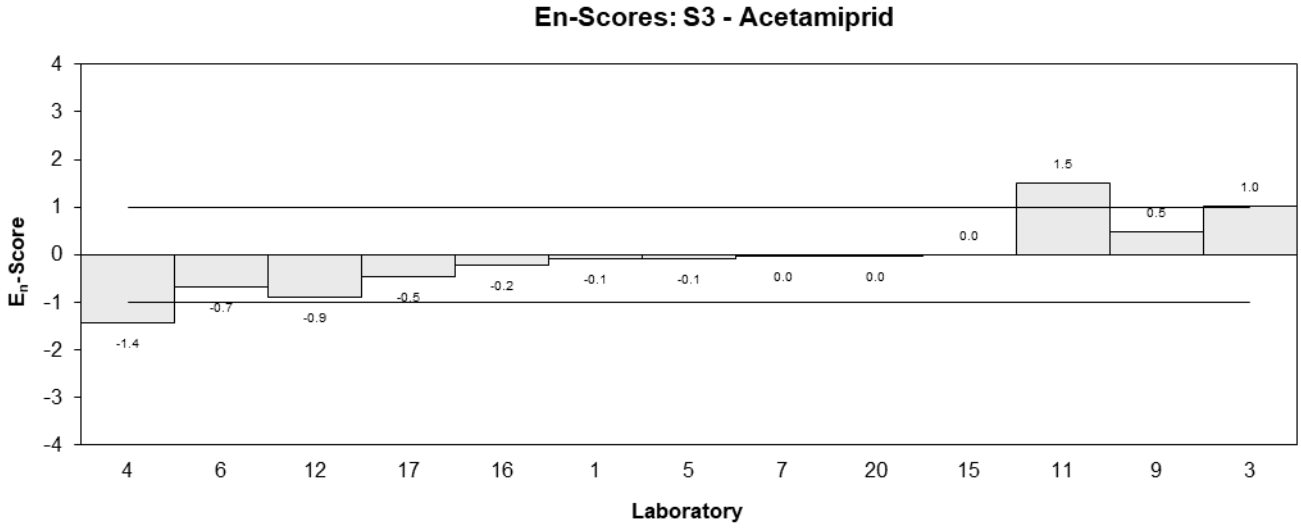

En-Scores: S3 - Acetamiprid
En-Score
-1.4 -0.7 -0.9 -0.5 -0.2 -0.1 -0.1 0.0 0.0 0.0 1.5 0.5 1.0
Laboratory
4 6 12 17 16 1 5 7 20 15 11 9 3

Figure 9

Table 13

Sample Details

Sample No.	S3
Matrix	Grape
Analyte	Bifenthrin
Unit	mg/kg

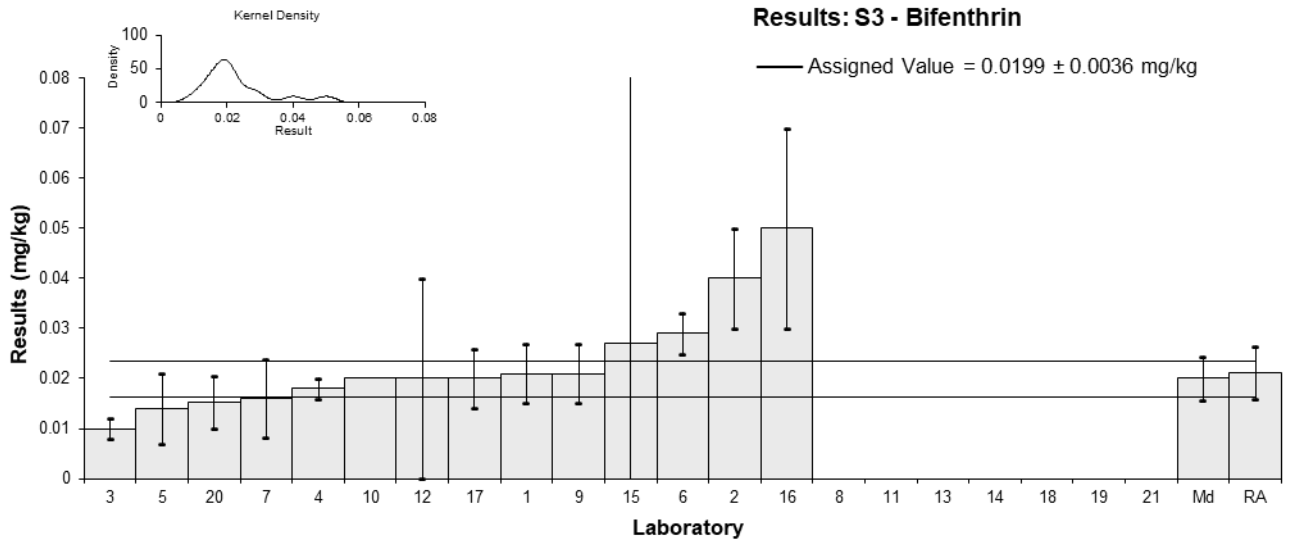
Participant Results

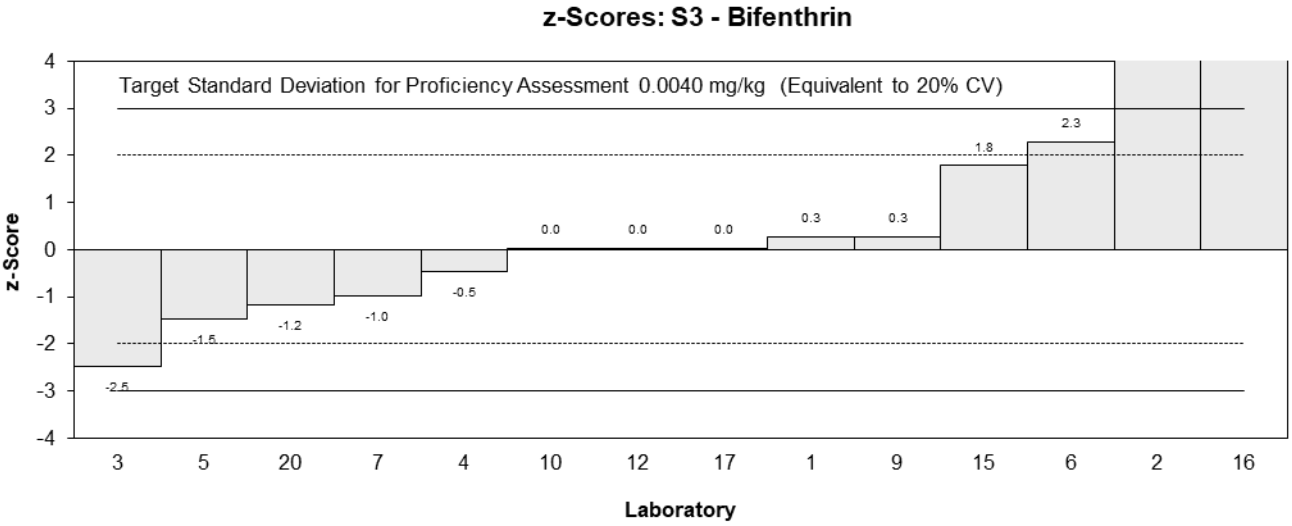
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.021	0.006	97	0.28	0.16
2*	0.04	0.01	55.00	5.05	1.89
3*	0.01	0.002	89	-2.49	-2.40
4	0.018	0.002	91	-0.48	-0.46
5	0.014	0.007	NR	-1.48	-0.75
6	0.029	0.0041	78	2.29	1.67
7	0.016	0.0079	NR	-0.98	-0.45
8	NT	NT	NT		
9	0.021	0.006	180	0.28	0.16
10	0.02	NR	105	0.03	0.03
11	<0.02	NR	NR		
12	0.02	0.02	108.94	0.03	0.00
13	NT	NT	NT		
14	NR	NR	NR		
15	0.027	50	94	1.78	0.00
16*	0.05	0.02	NR	7.56	1.48
17	0.020	0.006	80	0.03	0.01
18	<0.01	NR	105		
19	NR	NR	NR		
20	0.0152	0.0053	92	-1.18	-0.73
21	<0.01	NR	72		

* Outlier, see Section 4.2

Statistics

Assigned Value	0.0199	0.0036
Spike Value	Not Spiked	
Robust Average	0.0212	0.0053
Median	0.0200	0.0044
Mean	0.0229	
N	14	
Max	0.05	
Min	0.01	
Robust SD	0.0079	
Robust CV	37%	


Kernel Density
Density
Result
Results: S3 - Bifenthrin
Assigned Value = 0.0199 ± 0.0036 mg/kg
Results (mg/kg)
Laboratory
3 5 20 7 4 10 12 17 1 9 15 6 2 16 8 11 13 14 18 19 21 Md RA


z-Scores: S3 - Bifenthrin
Target Standard Deviation for Proficiency Assessment 0.0040 mg/kg (Equivalent to 20% CV)
z-Score
Laboratory
3 5 20 7 4 10 12 17 1 9 15 6 2 16

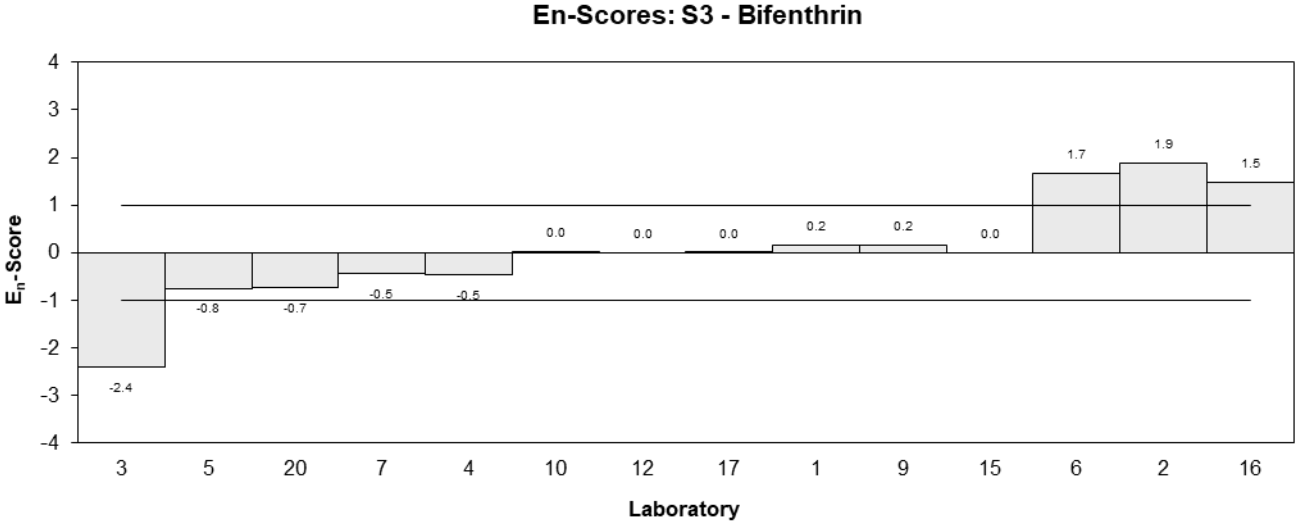

En-Scores: S3 - Bifenthrin
En-Score
Laboratory
3 5 20 7 4 10 12 17 1 9 15 6 2 16

Figure 10

Table 14

Sample Details

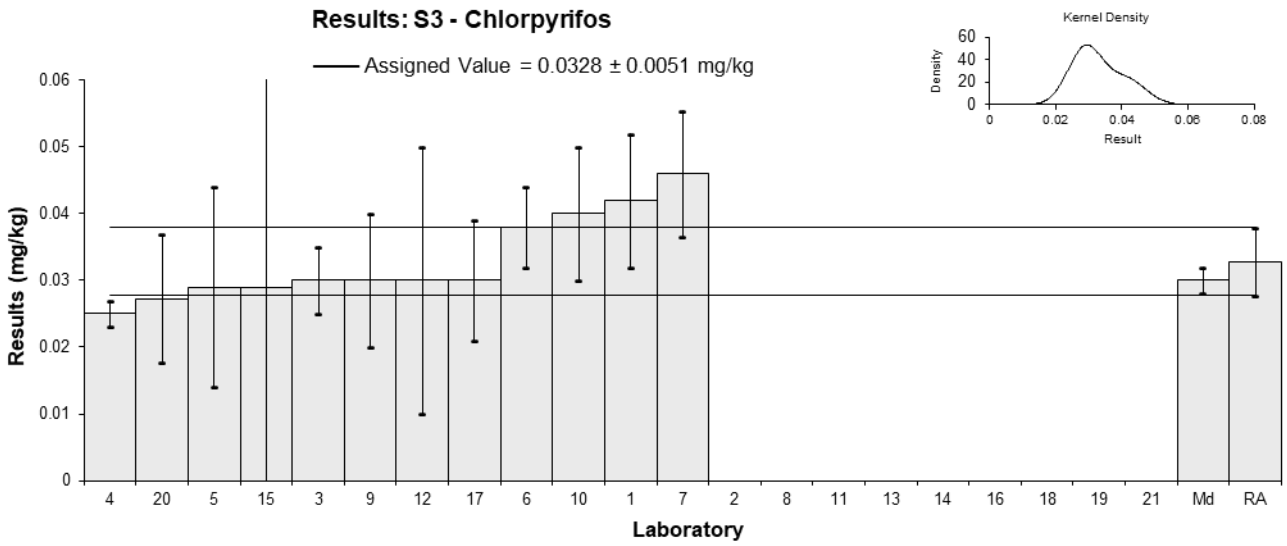
Sample No.	S3
Matrix	Grape
Analyte	Chlorpyrifos
Unit	mg/kg

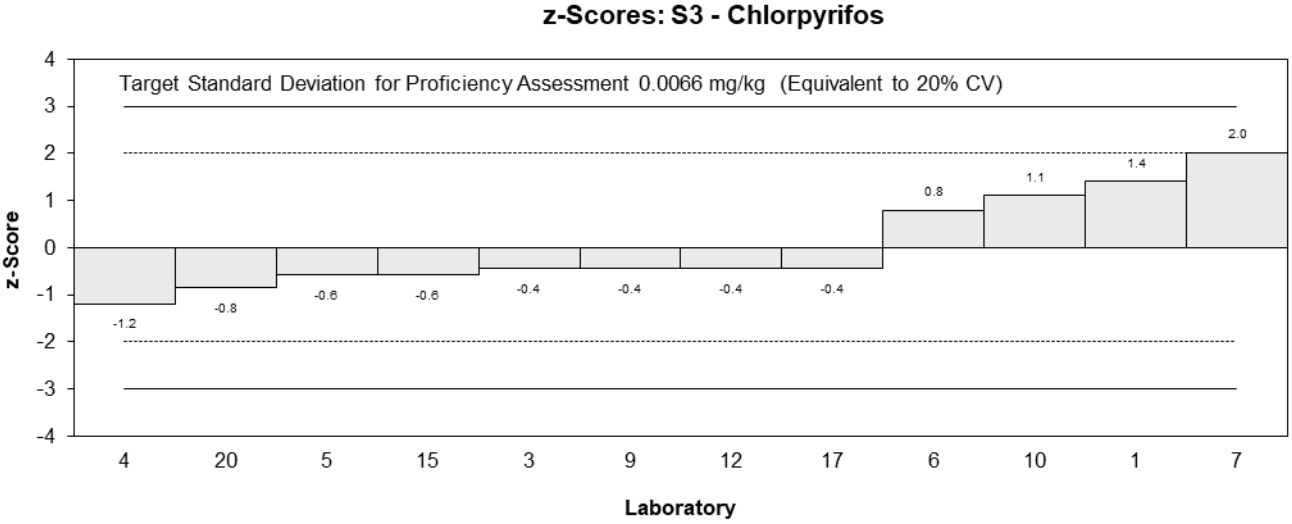
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.042	0.01	98	1.40	0.82
2	NR	NR	NR		
3	0.03	0.005	92	-0.43	-0.39
4	0.025	0.002	70	-1.19	-1.42
5	0.029	0.015	NR	-0.58	-0.24
6	0.038	0.006	79	0.79	0.66
7	0.046	0.0094	NR	2.01	1.23
8	NT	NT	NT		
9	0.03	0.01	100	-0.43	-0.25
10	0.04	0.01	87	1.10	0.64
11	<0.02	NR	NR		
12	0.03	0.02	88.58	-0.43	-0.14
13	NT	NT	NT		
14	NR	NR	NR		
15	0.029	50	115	-0.58	0.00
16	NR	NR	NR		
17	0.03	0.009	78	-0.43	-0.27
18	<0.01	NR	110		
19	NR	NR	NR		
20	0.0273	0.0096	97	-0.84	-0.51
21	<0.01	NR	105		

Statistics

Assigned Value	0.0328	0.0051
Spike Value	Not Spiked	
Robust Average	0.0328	0.0051
Median	0.0300	0.0020
Mean	0.0330	
N	12	
Max	0.046	
Min	0.025	
Robust SD	0.0071	
Robust CV	22%	


Results: S3 - Chlorpyrifos
Assigned Value = 0.0328 ± 0.0051 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
4 20 5 15 3 9 12 17 6 10 1 7 2 8 11 13 14 16 18 19 21 Md RA


z-Scores: S3 - Chlorpyrifos
Target Standard Deviation for Proficiency Assessment 0.0066 mg/kg (Equivalent to 20% CV)
z-Score
Laboratory
4 20 5 15 3 9 12 17 6 10 1 7
-1.2 -0.8 -0.6 -0.6 -0.4 -0.4 -0.4 -0.4 0.8 1.1 1.4 2.0

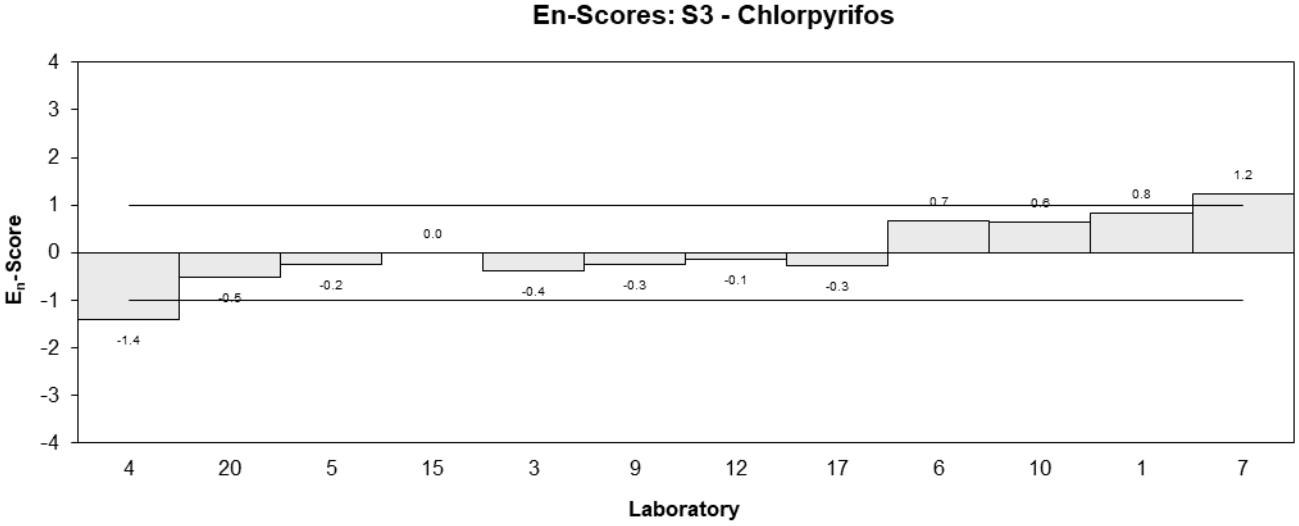

En-Scores: S3 - Chlorpyrifos
En-Score
Laboratory
4 20 5 15 3 9 12 17 6 10 1 7
-1.4 -0.5 -0.2 0.0 -0.4 -0.3 -0.1 -0.3 0.7 0.6 0.8 1.2

Figure 11

Table 15

Sample Details

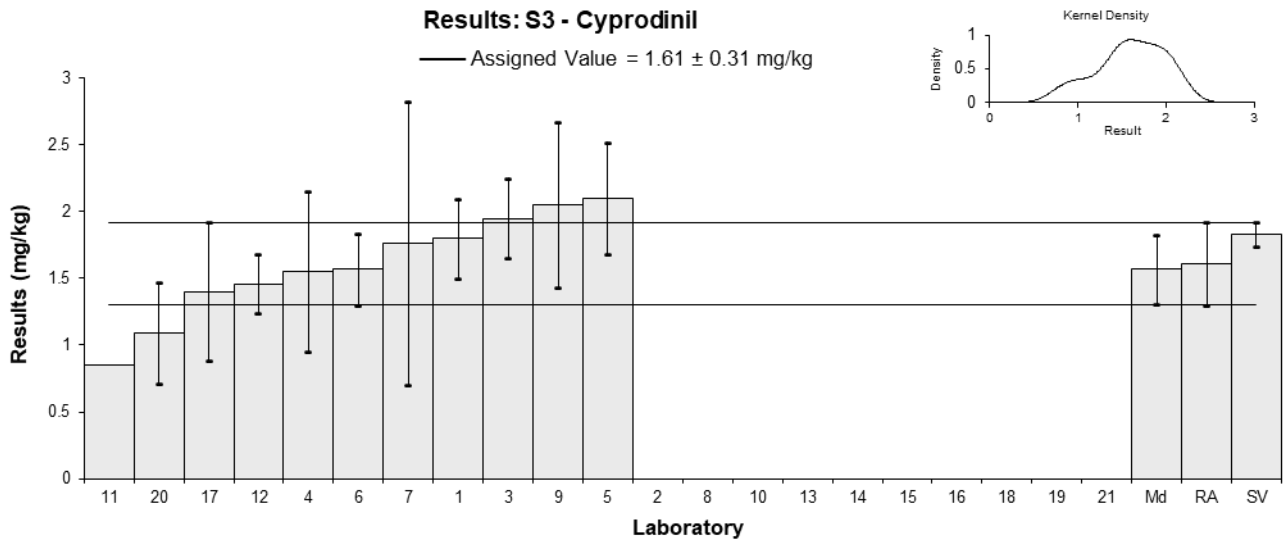
Sample No.	S3
Matrix	Grape
Analyte	Cyprodinil
Unit	mg/kg

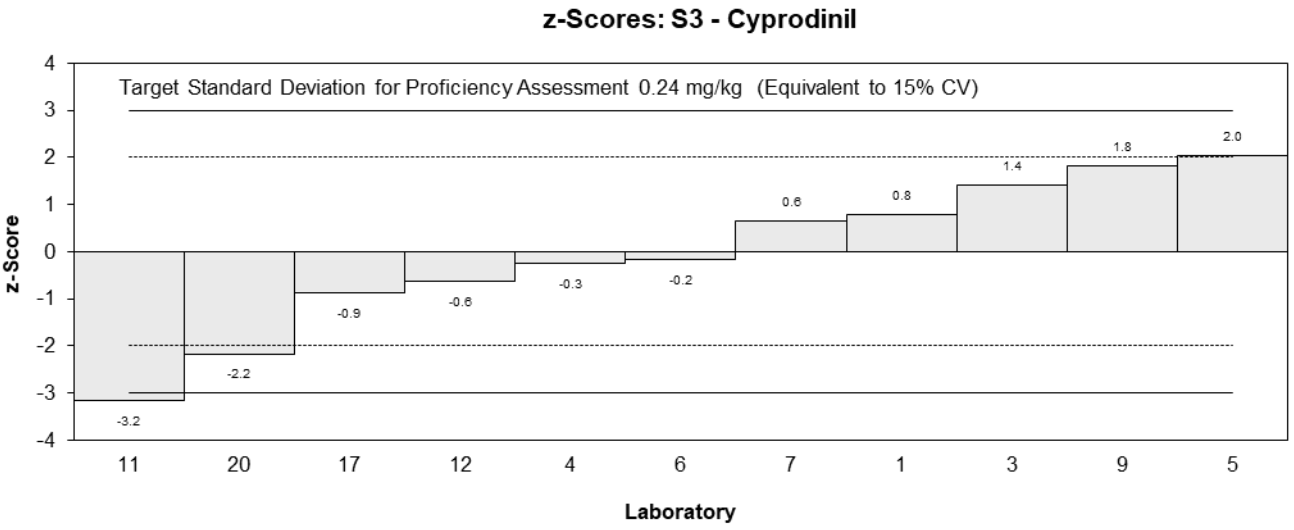
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	1.8	0.3	94	0.79	0.44
2	NT	NT	NT		
3	1.95	0.3	82	1.41	0.79
4	1.55	0.6	95	-0.25	-0.09
5	2.1	0.42	NR	2.03	0.94
6	1.569	0.27	82	-0.17	-0.10
7	1.7644	1.066	NR	0.64	0.14
8	NT	NT	NT		
9	2.05	0.62	87	1.82	0.63
10	NT	NT	NT		
11	0.847	NR	90	-3.16	-2.46
12	1.46	0.22	97.24	-0.62	-0.39
13	NT	NT	NT		
14	NT	NT	NT		
15	NT	NT	NT		
16	NT	NT	NT		
17	1.4	0.52	88	-0.87	-0.35
18	NT	NT	NT		
19	NT	NT	NT		
20	1.087	0.380	98	-2.17	-1.07
21	NT	NT	NT		

Statistics

Assigned Value	1.61	0.31
Spike Value	1.83	0.09
Robust Average	1.61	0.31
Median	1.57	0.26
Mean	1.60	
N	11	
Max	2.1	
Min	0.847	
Robust SD	0.42	
Robust CV	26%	


Results: S3 - Cyprodinil
Assigned Value = 1.61 ± 0.31 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
11 20 17 12 4 6 7 1 3 9 5 2 8 10 13 14 15 16 18 19 21 Md RA SV
Laboratory


z-Scores: S3 - Cyprodinil
Target Standard Deviation for Proficiency Assessment 0.24 mg/kg (Equivalent to 15% CV)
z-Score
-3.2 -2.2 -0.9 -0.6 -0.3 -0.2 0.6 0.8 1.4 1.8 2.0
11 20 17 12 4 6 7 1 3 9 5
Laboratory

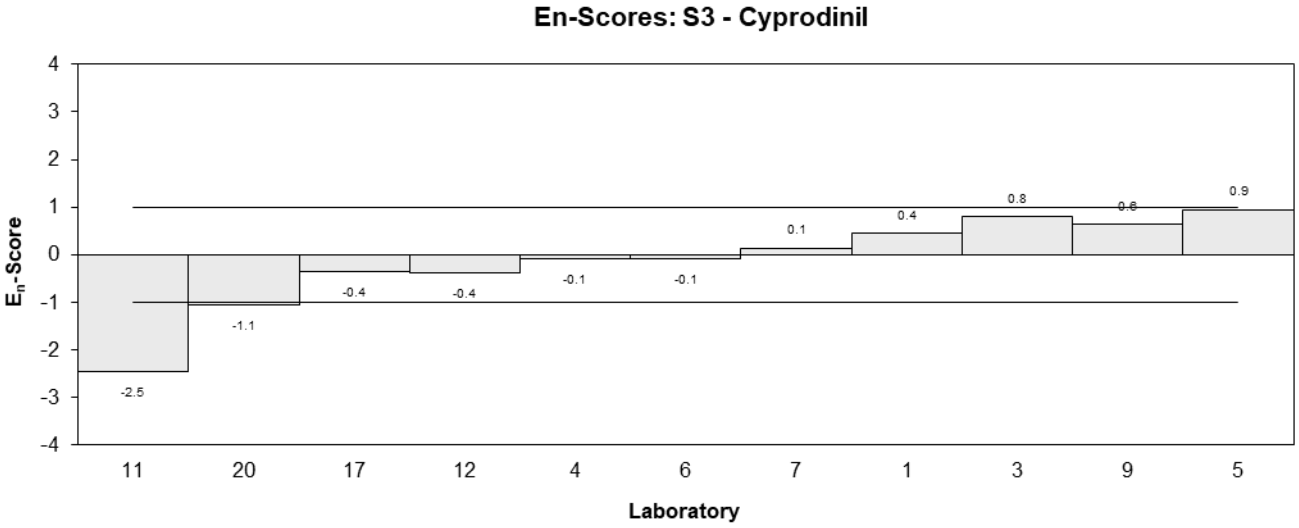

En-Scores: S3 - Cyprodinil
En-Score
-2.5 -1.1 -0.4 -0.4 -0.1 -0.1 0.1 0.4 0.8 0.6 0.9
11 20 17 12 4 6 7 1 3 9 5
Laboratory

Figure 12

Table 16

Sample Details

Sample No.	S3
Matrix	Grape
Analyte	Fenhexamid
Unit	mg/kg

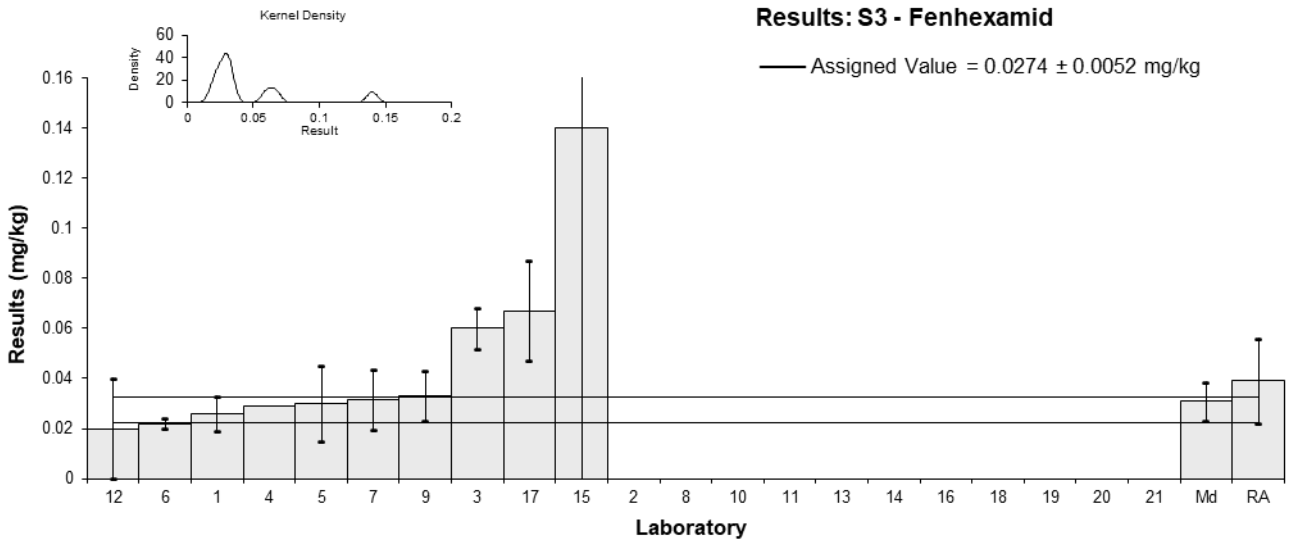
Participant Results

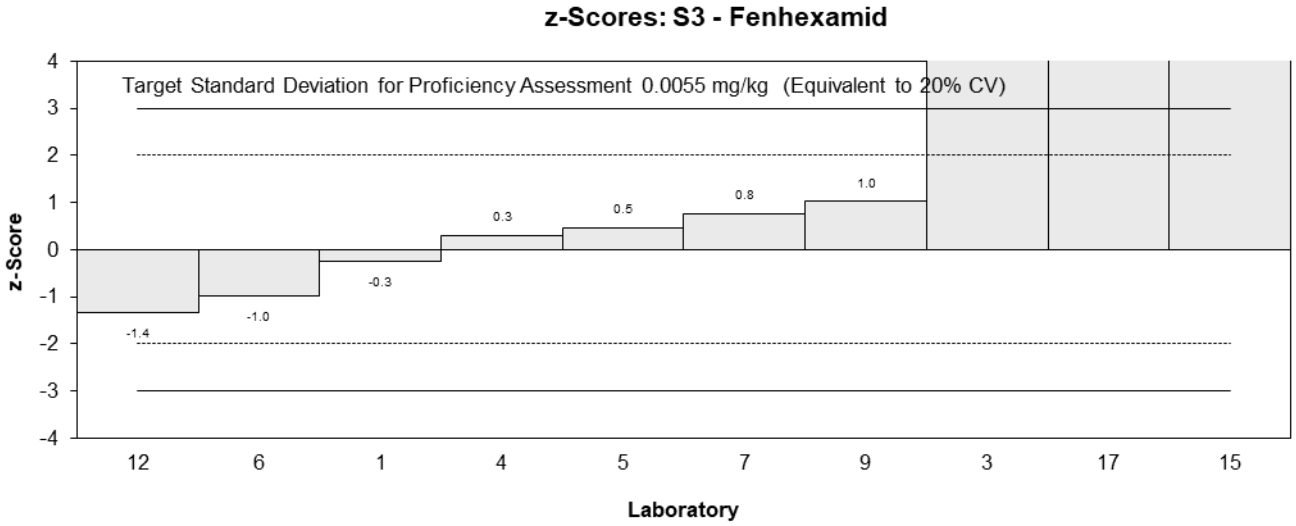
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.026	0.007	92	-0.26	-0.16
2	NT	NT	NT		
3*	0.06	0.008	77	5.95	3.42
4	0.029	NR	80	0.29	0.31
5	0.03	0.015	NR	0.47	0.16
6	0.022	0.002	84	-0.99	-0.97
7	0.0315	0.012	NR	0.75	0.31
8	NT	NT	NT		
9	0.033	0.010	67	1.02	0.50
10	NT	NT	NT		
11	<0.02	NR	NR		
12	0.02	0.02	107.33	-1.35	-0.36
13	NT	NT	NT		
14	NT	NT	NT		
15*	0.14	50	117	20.55	0.00
16	NT	NT	NT		
17*	0.067	0.02	87	7.23	1.92
18	NT	NT	NT		
19	NT	NT	NT		
20	NT	NT	NT		
21	NT	NT	NT		

* Outlier, see Section 4.2

Statistics

Assigned Value	0.0274	0.0052
Spike Value	Not Spiked	
Robust Average	0.039	0.017
Median	0.0308	0.0079
Mean	0.046	
N	10	
Max	0.14	
Min	0.02	
Robust SD	0.022	
Robust CV	57%	


Kernel Density
Density
Result
Results: S3 - Fenhexamid
Assigned Value = 0.0274 ± 0.0052 mg/kg
Results (mg/kg)
Laboratory
12 6 1 4 5 7 9 3 17 15 2 8 10 11 13 14 16 18 19 20 21 Md RA


z-Scores: S3 - Fenhexamid
Target Standard Deviation for Proficiency Assessment 0.0055 mg/kg (Equivalent to 20% CV)
z-Score
-1.4
-1.0
-0.3
0.3
0.5
0.8
1.0
Laboratory
12 6 1 4 5 7 9 3 17 15

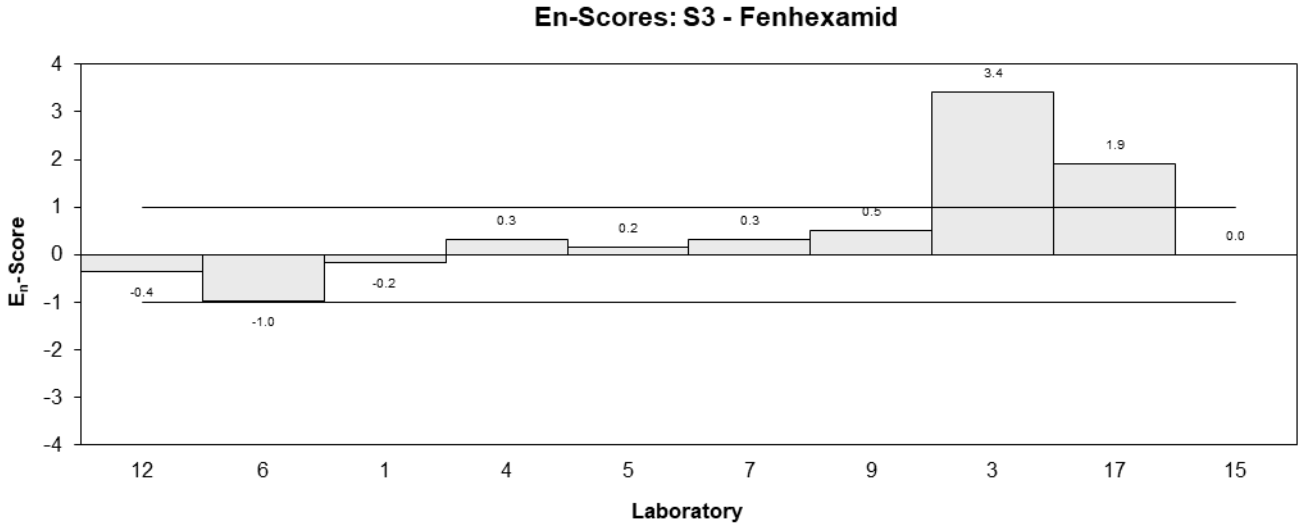

En-Scores: S3 - Fenhexamid
En-Score
-0.4
-1.0
-0.2
0.3
0.2
0.3
0.5
3.4
1.9
0.0
Laboratory
12 6 1 4 5 7 9 3 17 15

Figure 13

Table 17

Sample Details

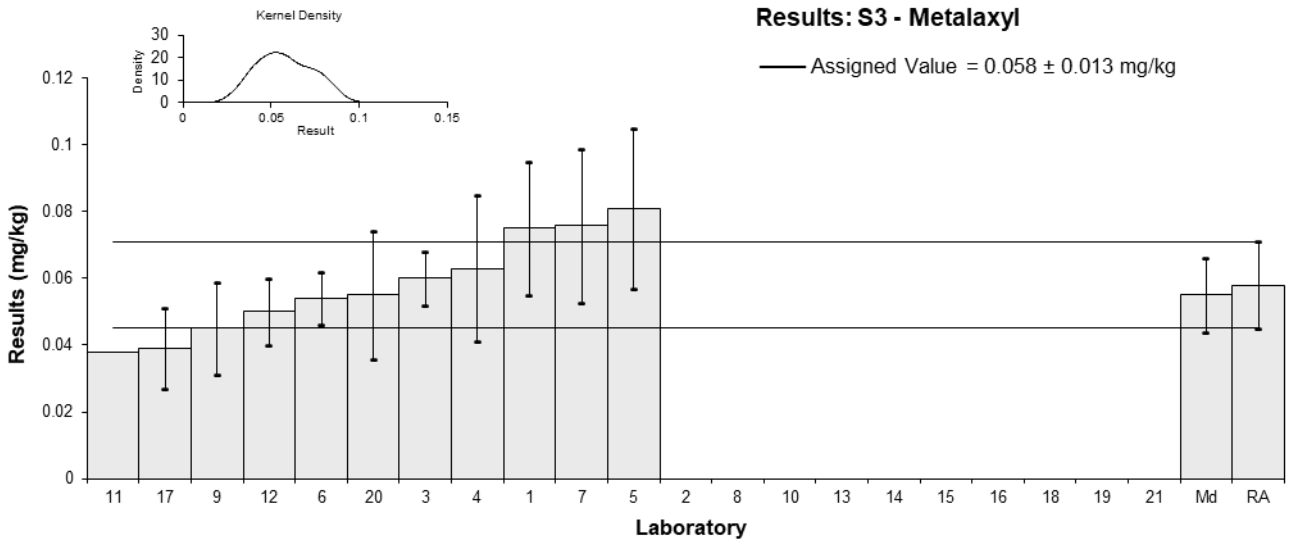
Sample No.	S3
Matrix	Grape
Analyte	Metalaxyl
Unit	mg/kg

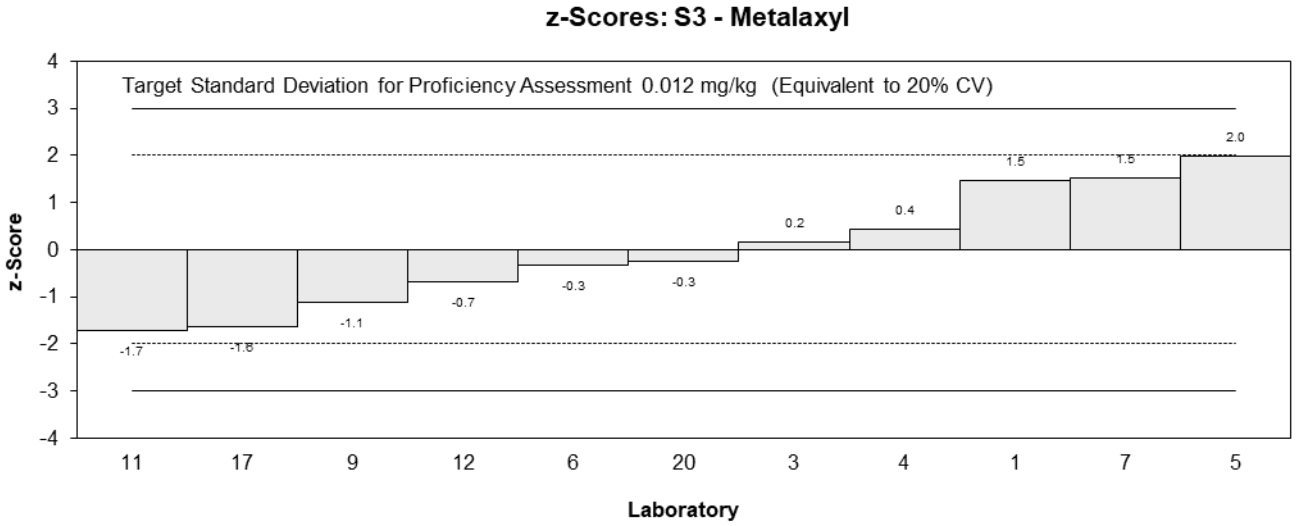
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.075	0.02	87	1.47	0.71
2	NT	NT	NT		
3	0.06	0.008	91	0.17	0.13
4	0.063	0.022	85	0.43	0.20
5	0.081	0.024	NR	1.98	0.84
6	0.054	0.008	85	-0.34	-0.26
7	0.0758	0.023	NR	1.53	0.67
8	NT	NT	NT		
9	0.045	0.014	60	-1.12	-0.68
10	NT	NT	NT		
11	0.038	NR	72	-1.72	-1.54
12	0.05	0.01	96.84	-0.69	-0.49
13	NT	NT	NT		
14	NT	NT	NT		
15	NT	NT	NT		
16	NT	NT	NT		
17	0.039	0.012	89	-1.64	-1.07
18	NT	NT	NT		
19	NR	NR	NR		
20	0.0551	0.0193	91	-0.25	-0.12
21	NT	NT	NT		

Statistics

Assigned Value	0.058	0.013
Spike Value	Not Spiked	
Robust Average	0.058	0.013
Median	0.055	0.011
Mean	0.0578	
N	11	
Max	0.081	
Min	0.038	
Robust SD	0.017	
Robust CV	29%	


Results: S3 - Metalaxyl
Assigned Value = 0.058 ± 0.013 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
11 17 9 12 6 20 3 4 1 7 5 2 8 10 13 14 15 16 18 19 21 Md RA


z-Scores: S3 - Metalaxyl
Target Standard Deviation for Proficiency Assessment 0.012 mg/kg (Equivalent to 20% CV)
z-Score
Laboratory
11 17 9 12 6 20 3 4 1 7 5
-1.7 -1.6 -1.1 -0.7 -0.3 -0.3 0.2 0.4 1.5 1.5 2.0

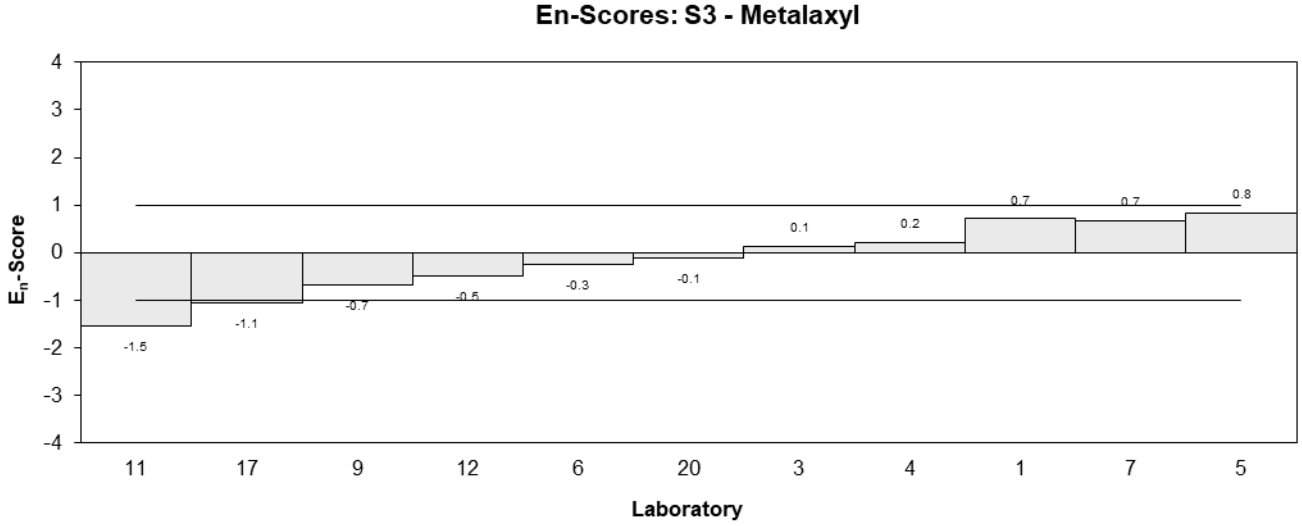

En-Scores: S3 - Metalaxyl
En-Score
Laboratory
11 17 9 12 6 20 3 4 1 7 5
-1.5 -1.1 -0.7 -0.5 -0.3 -0.1 0.1 0.2 0.7 0.7 0.8

Figure 14

Table 18

Sample Details

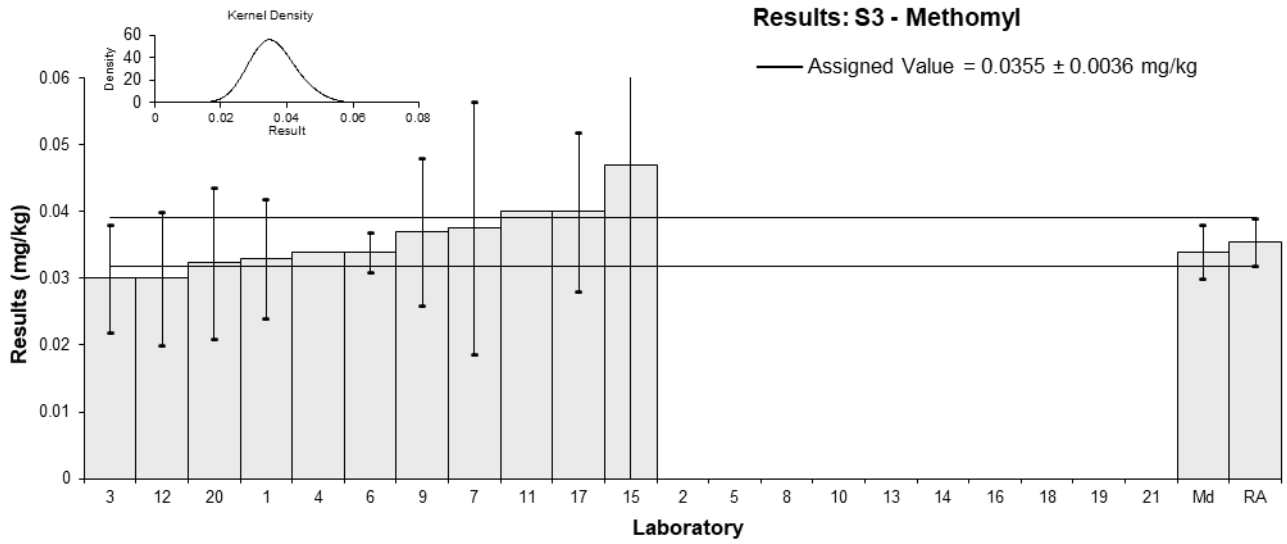
Sample No.	S3
Matrix	Grape
Analyte	Methomyl
Unit	mg/kg

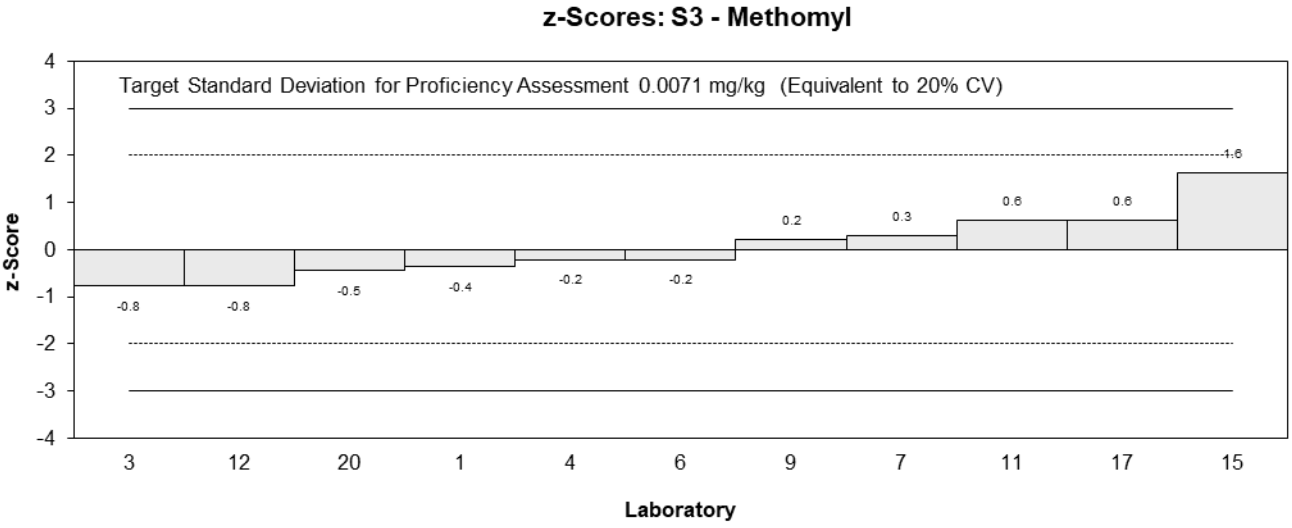
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.033	0.009	95	-0.35	-0.26
2	NT	NT	NT		
3	0.03	0.008	86	-0.77	-0.63
4	0.034	NR	101	-0.21	-0.42
5	NR	NR	NR		
6	0.034	0.003	79	-0.21	-0.32
7	0.0376	0.019	NR	0.30	0.11
8	NT	NT	NT		
9	0.037	0.011	86	0.21	0.13
10	NT	NT	NT		
11	0.040	NR	84	0.63	1.25
12	0.03	0.01	98.8	-0.77	-0.52
13	NT	NT	NT		
14	NT	NT	NT		
15	0.047	50	147	1.62	0.00
16	NT	NT	NT		
17	0.040	0.012	91	0.63	0.36
18	NT	NT	NT		
19	NT	NT	NT		
20	0.0323	0.0113	92	-0.45	-0.27
21	NT	NT	NT		

Statistics

Assigned Value	0.0355	0.0036
Spike Value	Not Spiked	
Robust Average	0.0355	0.0036
Median	0.0340	0.0040
Mean	0.0359	
N	11	
Max	0.047	
Min	0.03	
Robust SD	0.0048	
Robust CV	14%	


Kernel Density
Density
Result
Results: S3 - Methomyl
Assigned Value = 0.0355 ± 0.0036 mg/kg
Results (mg/kg)
Laboratory
3 12 20 1 4 6 9 7 11 17 15 2 5 8 10 13 14 16 18 19 21 Md RA


z-Scores: S3 - Methomyl
Target Standard Deviation for Proficiency Assessment 0.0071 mg/kg (Equivalent to 20% CV)
z-Score
Laboratory
3 12 20 1 4 6 9 7 11 17 15
-0.8 -0.8 -0.5 -0.4 -0.2 -0.2 0.2 0.3 0.6 0.6 1.6

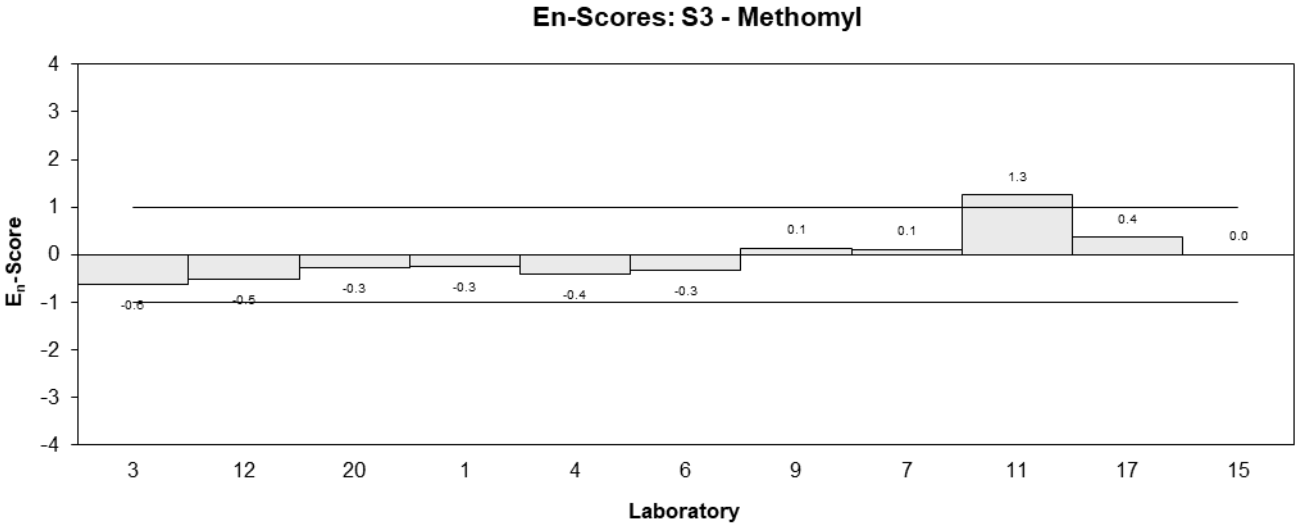

En-Scores: S3 - Methomyl
En-Score
Laboratory
3 12 20 1 4 6 9 7 11 17 15
-0.6 -0.5 -0.3 -0.3 -0.4 -0.3 0.1 0.1 1.3 0.4 0.0

Figure 15

Table 19

Sample Details

Sample No.	S3
Matrix	Grape
Analyte	Metrafenone
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	1.0	0.2	98
2	NT	NT	NT
3	NT	NT	NT
4	NT	NT	NT
5	1.2	0.24	NR
6	0.6	0.15	84
7	NT	NT	NT
8	NT	NT	NT
9	1.18	0.35	100
10	NT	NT	NT
11	0.141	NR	107
12	1.06	0.11	102.97
13	NT	NT	NT
14	NT	NT	NT
15	0.562	50	100
16	NT	NT	NT
17	0.69	0.21	112
18	NT	NT	NT
19	NT	NT	NT
20	0.463	0.162	89
21	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	1.10	0.05
Robust Average	0.77	0.34
Median	0.69	0.38
Mean	0.77	
N	9	
Max	1.2	
Min	0.141	
Robust SD	0.41	
Robust CV	53%	

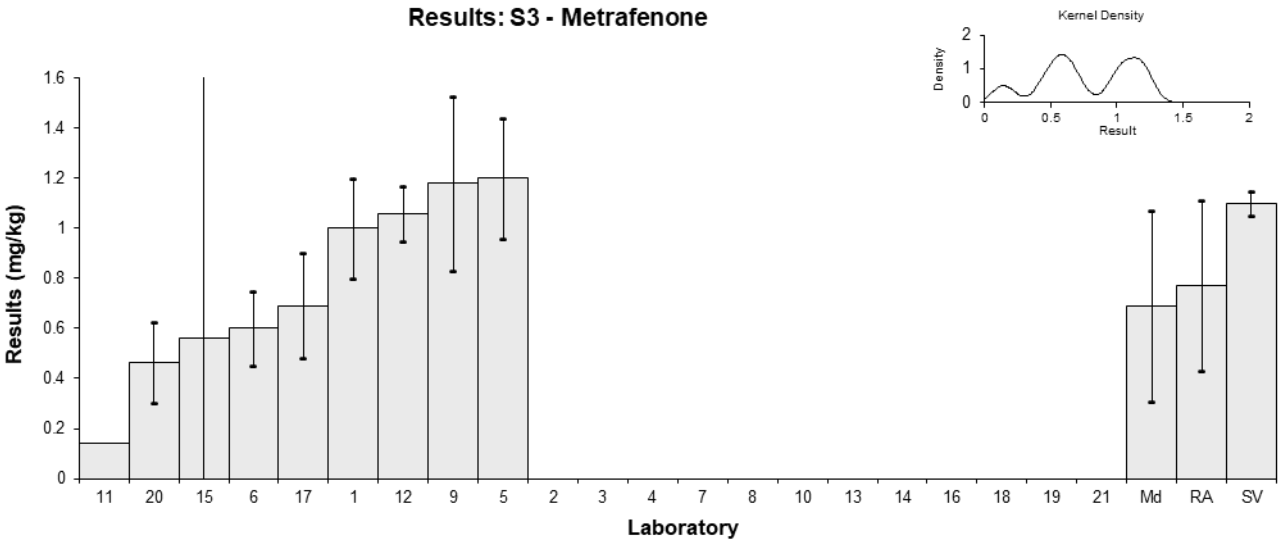

Results: S3 - Metrafenone
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
11
20
15
6
17
1
12
9
5
2
3
4
7
8
10
13
14
16
18
19
21
Md
RA
SV

Figure 16

Table 20

Sample Details

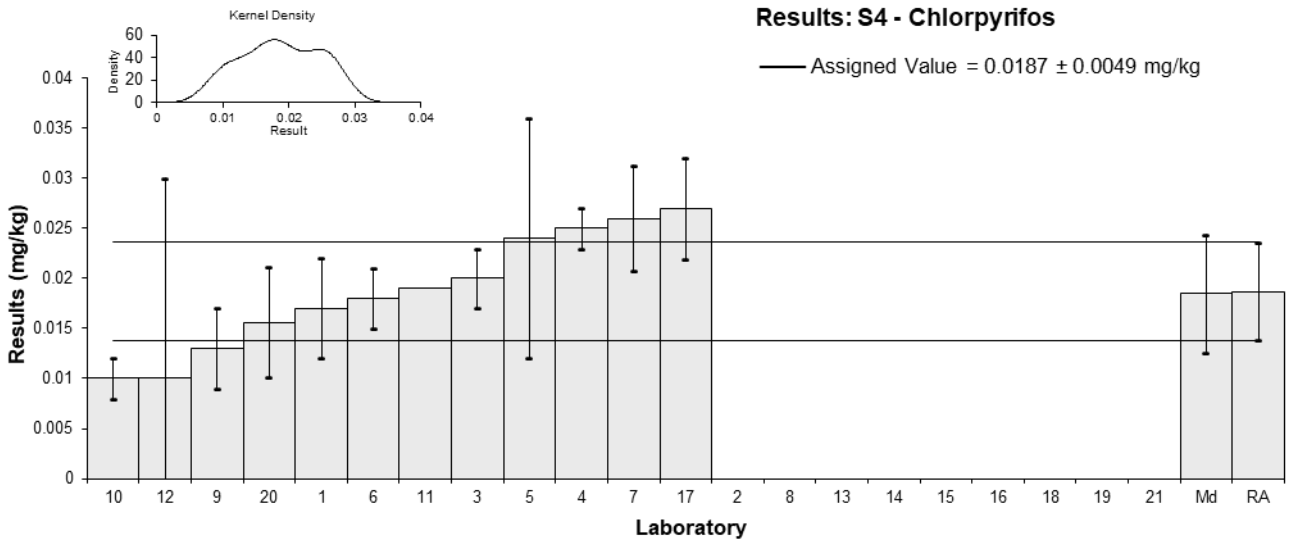
Sample No.	S4
Matrix	Coriander
Analyte	Chlorpyrifos
Unit	mg/kg

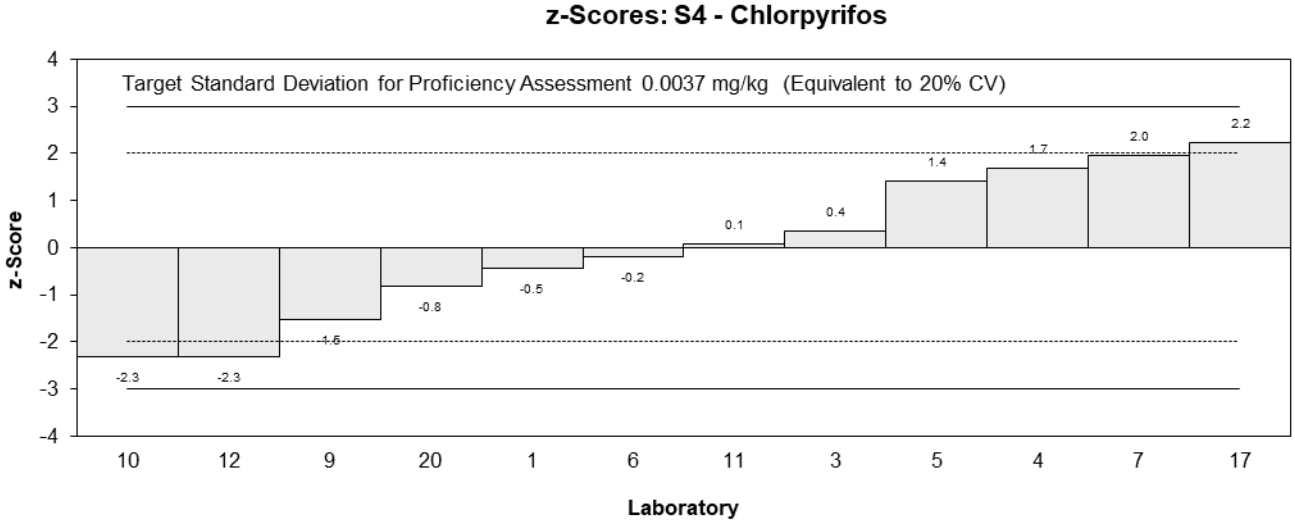
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.017	0.005	99	-0.45	-0.24
2	NR	NR	NR		
3	0.02	0.003	92	0.35	0.23
4	0.025	0.002	73	1.68	1.19
5	0.024	0.012	NR	1.42	0.41
6	0.018	0.003	103	-0.19	-0.12
7	0.026	0.0053	NR	1.95	1.01
8	NT	NT	NT		
9	0.013	0.004	100	-1.52	-0.90
10	0.01	0.002	87	-2.33	-1.64
11	0.019	NR	138	0.08	0.06
12	0.01	0.02	81.73	-2.33	-0.42
13	NT	NT	NT		
14	NR	NR	NR		
15	NT	NT	NT		
16	NR	NR	NR		
17	0.027	0.0051	73	2.22	1.17
18	<0.01	NR	76		
19	NR	NR	NR		
20	0.0156	0.0055	98	-0.83	-0.42
21	<0.01	NR	110		

Statistics

Assigned Value	0.0187	0.0049
Spike Value	Not Spiked	
Robust Average	0.0187	0.0049
Median	0.0185	0.0059
Mean	0.0187	
N	12	
Max	0.027	
Min	0.01	
Robust SD	0.0067	
Robust CV	36%	


Kernel Density
Density
Result
Results: S4 - Chlorpyrifos
Assigned Value = 0.0187 ± 0.0049 mg/kg
Results (mg/kg)
Laboratory
10 12 9 20 1 6 11 3 5 4 7 17 2 8 13 14 15 16 18 19 21 Md RA


z-Scores: S4 - Chlorpyrifos
Target Standard Deviation for Proficiency Assessment 0.0037 mg/kg (Equivalent to 20% CV)
z-Score
-2.3 -2.3 -1.5 -0.8 -0.5 -0.2 0.1 0.4 1.4 1.7 2.0 2.2
Laboratory
10 12 9 20 1 6 11 3 5 4 7 17

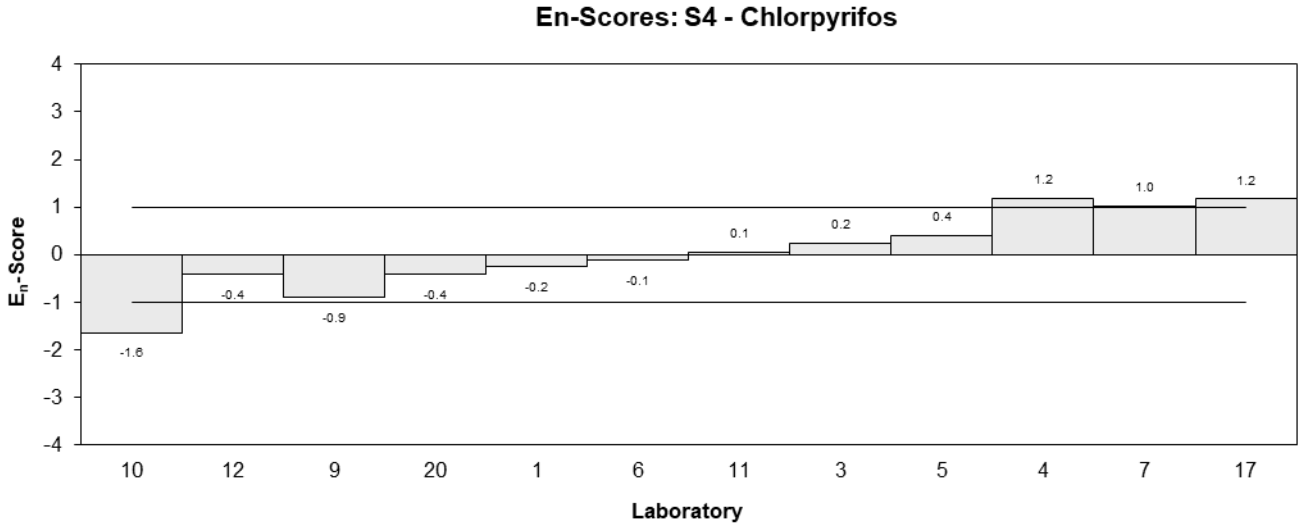

En-Scores: S4 - Chlorpyrifos
En-Score
-1.6 -0.4 -0.9 -0.4 -0.2 -0.1 0.1 0.2 0.4 1.2 1.0 1.2
Laboratory
10 12 9 20 1 6 11 3 5 4 7 17

Figure 17

Table 21

Sample Details

Sample No.	S4
Matrix	Coriander
Analyte	Cypermethrin
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	0.076	0.02	99
2	NR	NR	NR
3	0.14	0.02	94
4	NR	NR	NR
5	0.05	0.015	NR
6	0.016	0.003	102
7	0.211	0.062	NR
8	NT	NT	NT
9	0.118	0.035	410
10	NR	NR	NR
11	0.098	NR	67
12	< 0.05	NR	NR
13	NT	NT	NT
14	NR	NR	NR
15	NT	NT	NT
16	NR	NR	NR
17	0.04	0.012	111
18	0.02	0.01	111
19	NR	NR	NR
20	0.0428	0.0150	104
21	<0.01	NR	72

Statistics

Assigned Value	Not Set	
Spike Value	Not Spiked	
Robust Average	0.076	0.046
Median	0.063	0.046
Mean	0.081	
N	10	
Max	0.211	
Min	0.016	
Robust SD	0.058	
Robust CV	76%	

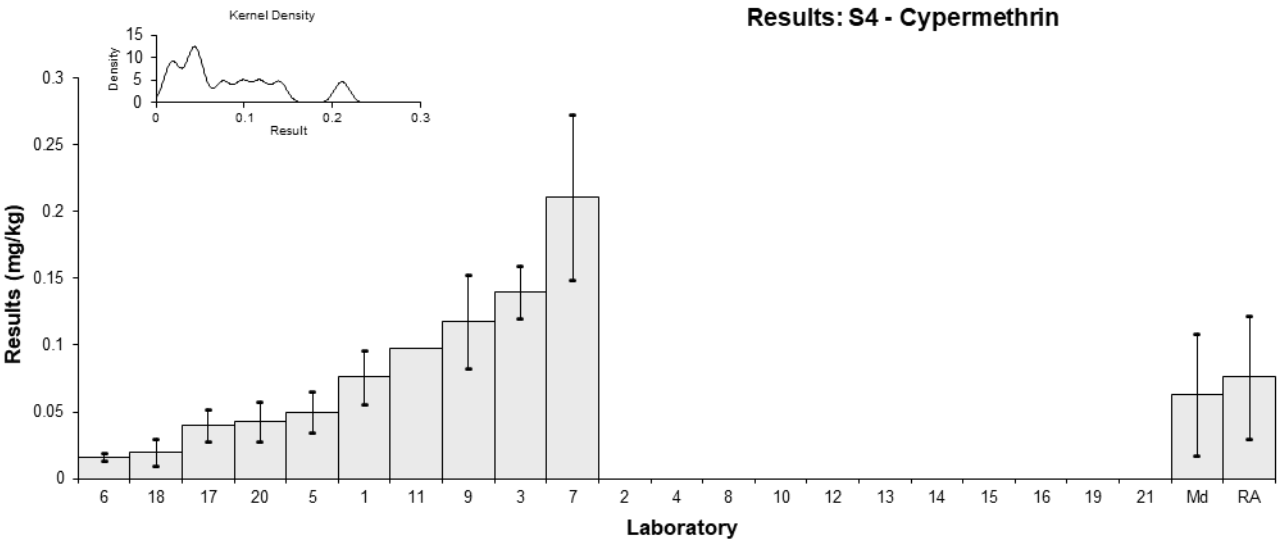

Results: S4 - Cypermethrin
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
6
18
17
20
5
1
11
9
3
7
2
4
8
10
12
13
14
15
16
19
21
Md
RA

Figure 18

Table 22

Sample Details

Sample No.	S4
Matrix	Coriander
Analyte	Cyprodinil
Unit	mg/kg

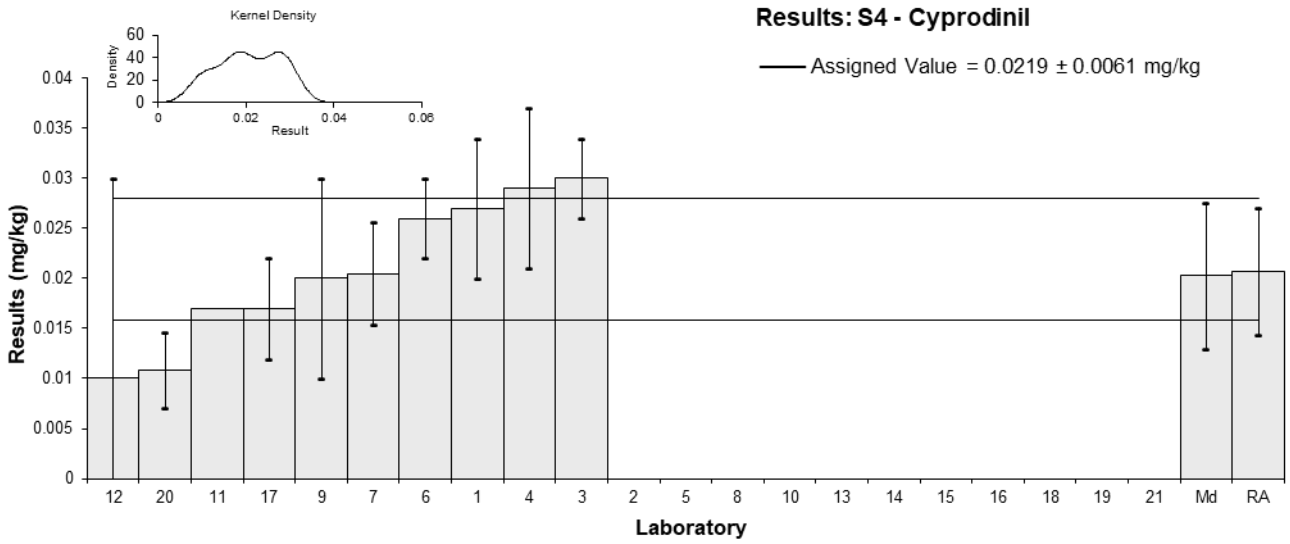
Participant Results

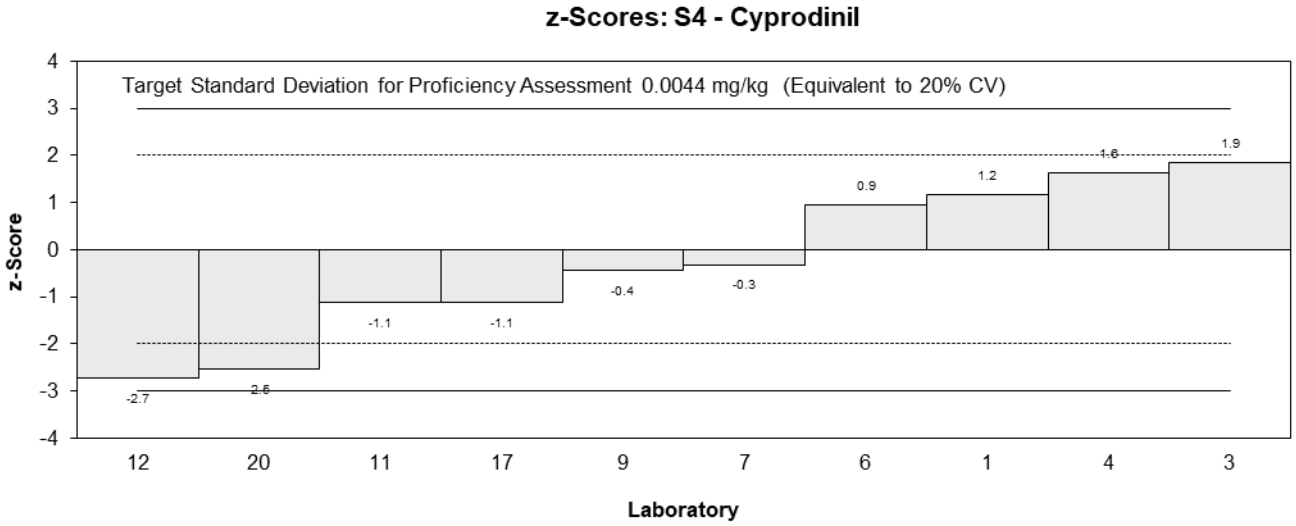
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.027	0.007	82	1.16	0.55
2	NT	NT	NT		
3	0.03	0.004	98	1.85	1.11
4	0.029	0.008	110	1.62	0.71
5	NR	NR	NR		
6	0.026	0.004	94	0.94	0.56
7	0.0205	0.0051	NR	-0.32	-0.18
8	NT	NT	NT		
9	0.02	0.01	80	-0.43	-0.16
10	NT	NT	NT		
11	0.017	NR	115	-1.12	-0.80
12*	0.01	0.02	85.19	-2.72	-0.57
13	NT	NT	NT		
14	NT	NT	NT		
15	NT	NT	NT		
16	NT	NT	NT		
17	0.017	0.0051	73	-1.12	-0.62
18	NT	NT	NT		
19	NT	NT	NT		
20	0.0108	0.0038	98	-2.53	-1.54
21	NT	NT	NT		

* Outlier, see Section 4.2

Statistics

Assigned Value	0.0219	0.0061
Spike Value	Not Spiked	
Robust Average	0.0207	0.0064
Median	0.0203	0.0073
Mean	0.0207	
N	10	
Max	0.03	
Min	0.01	
Robust SD	0.0081	
Robust CV	39%	


Results: S4 - Cyprodinil
Assigned Value = 0.0219 ± 0.0061 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
12 20 11 17 9 7 6 1 4 3 2 5 8 10 13 14 15 16 18 19 21 Md RA


z-Scores: S4 - Cyprodinil
Target Standard Deviation for Proficiency Assessment 0.0044 mg/kg (Equivalent to 20% CV)
z-Score
-2.7
-2.6
-1.1
-1.1
-0.4
-0.3
0.9
1.2
1.6
1.9
Laboratory
12 20 11 17 9 7 6 1 4 3

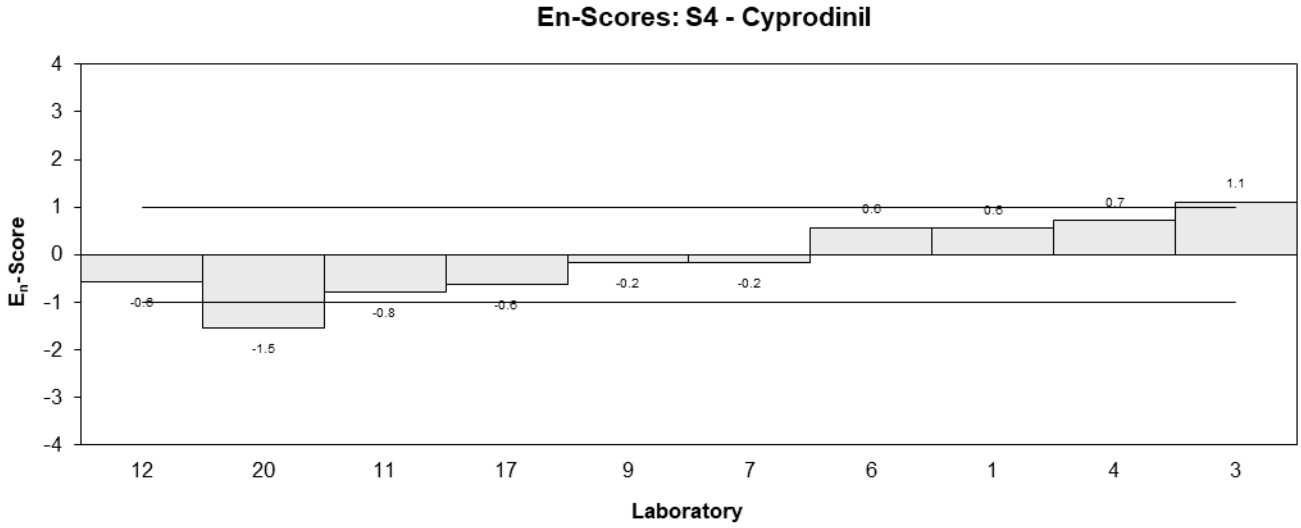

En-Scores: S4 - Cyprodinil
En-Score
-0.6
-1.5
-0.8
-0.6
-0.2
-0.2
0.6
0.6
0.7
1.1
Laboratory
12 20 11 17 9 7 6 1 4 3

Figure 19

Table 23

Sample Details

Sample No.	S4
Matrix	Coriander
Analyte	Fipronil
Unit	mg/kg

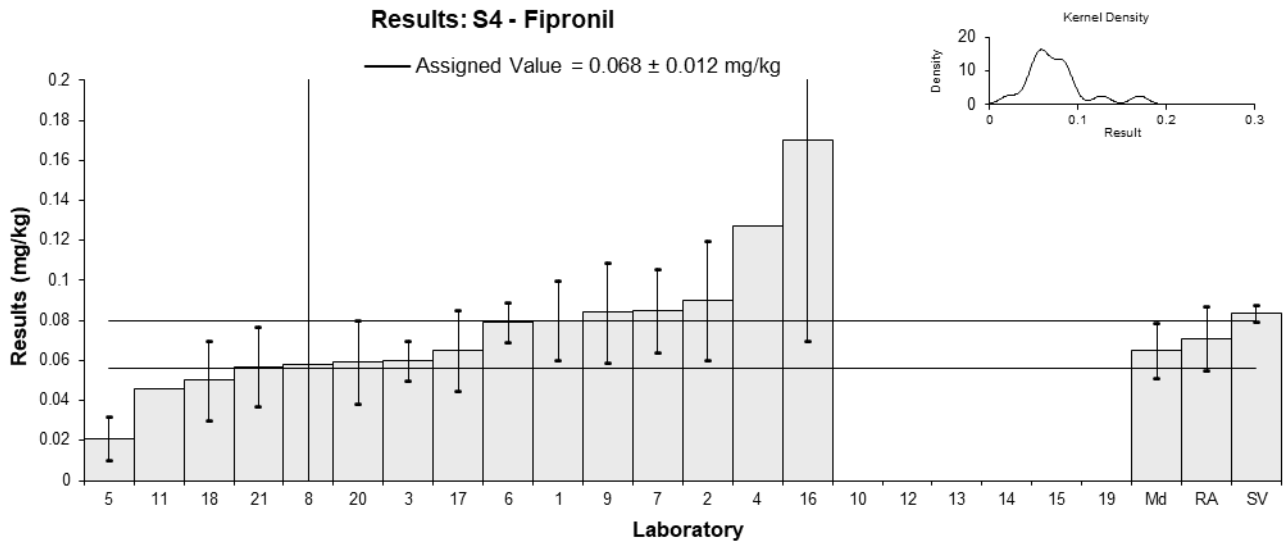
Participant Results

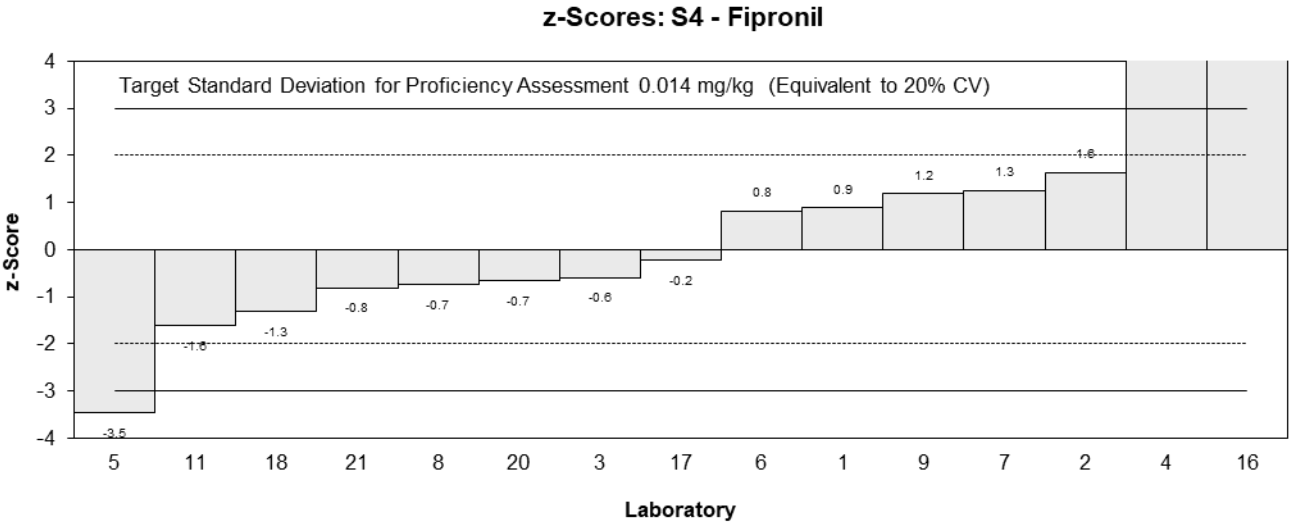
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.080	0.02	92	0.88	0.51
2	0.09	0.03	89.66	1.62	0.68
3	0.06	0.01	100	-0.59	-0.51
4*	0.127	NR	106	4.34	4.92
5*	0.021	0.011	NR	-3.46	-2.89
6	0.079	0.01	102	0.81	0.70
7	0.085	0.021	NR	1.25	0.70
8	0.058	0.184	114	-0.74	-0.05
9	0.084	0.025	92	1.18	0.58
10	NT	NT	NT		
11	0.046	NR	96	-1.62	-1.83
12	NT	NT	NT		
13	NT	NT	NT		
14	NT	NT	NT		
15	NT	NT	NT		
16*	0.17	0.1	NR	7.50	1.01
17	0.065	0.02	97	-0.22	-0.13
18	0.05	0.02	118	-1.32	-0.77
19	NR	NR	NR		
20	0.0592	0.0207	95	-0.65	-0.37
21	0.057	0.02	117	-0.81	-0.47

* Outlier, see Section 4.2

Statistics

Assigned Value	0.068	0.012
Spike Value	0.0835	0.0042
Robust Average	0.071	0.016
Median	0.065	0.014
Mean	0.075	
N	15	
Max	0.17	
Min	0.021	
Robust SD	0.025	
Robust CV	35%	


Results: S4 - Fipronil
Assigned Value = 0.068 ± 0.012 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
5 11 18 21 8 20 3 17 6 1 9 7 2 4 16 10 12 13 14 15 19 Md RA SV


z-Scores: S4 - Fipronil
Target Standard Deviation for Proficiency Assessment 0.014 mg/kg (Equivalent to 20% CV)
z-Score
-3.5 -1.6 -1.3 -0.8 -0.7 -0.7 -0.6 -0.2 0.8 0.9 1.2 1.3 1.6
Laboratory
5 11 18 21 8 20 3 17 6 1 9 7 2 4 16

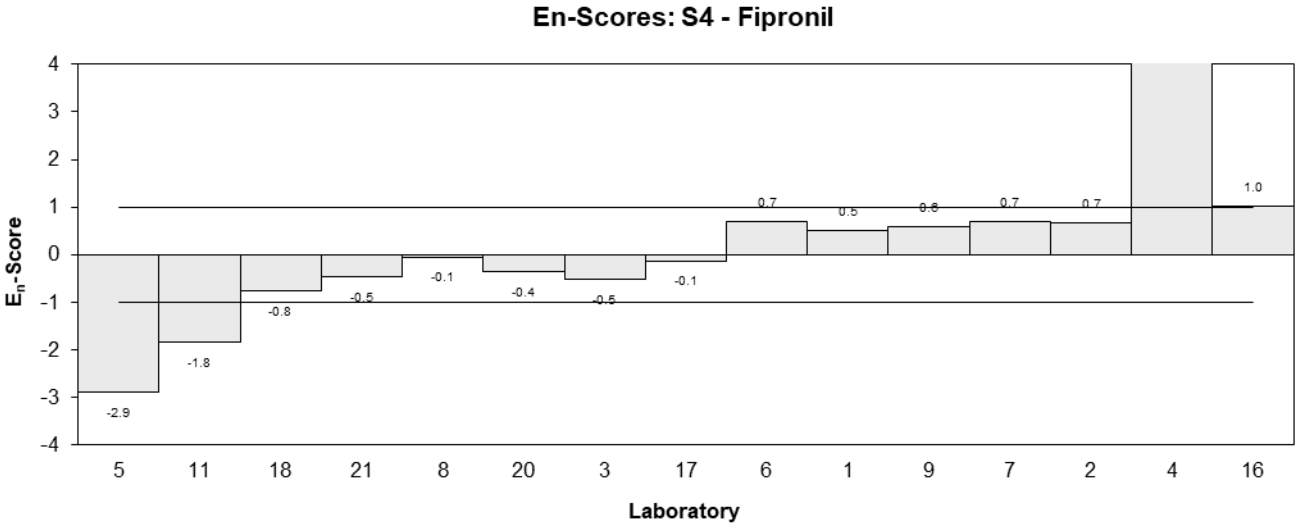

En-Scores: S4 - Fipronil
En-Score
-2.9 -1.8 -0.8 -0.5 -0.1 -0.4 -0.5 -0.1 0.7 0.5 0.6 0.7 0.7 1.0
Laboratory
5 11 18 21 8 20 3 17 6 1 9 7 2 4 16

Figure 20

Table 24

Sample Details

Sample No.	S4
Matrix	Coriander
Analyte	Iprodione
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	NR	NR	NR
2	NR	NR	NR
3	0.03	0.005	88
4	0.086	0.012	81
5	0.11	0.022	NR
6	0.04	0.006	112
7	NT	NT	NT
8	NT	NT	NT
9	0.16	NR	275
10	NT	NT	NT
11	<0.02	NR	NR
12	< 0.05	NR	NR
13	0.0279	0.0060	132.1
14	NT	NT	NT
15	NT	NT	NT
16	0.16	0.09	NR
17	0.034	0.012	102
18	<0.01	NR	140
19	NT	NT	NT
20	0.0561	0.0196	85
21	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	0.0706	0.0035
Robust Average	0.078	0.051
Median	0.056	0.035
Mean	0.078	
N	9	
Max	0.16	
Min	0.0279	
Robust SD	0.061	
Robust CV	78%	

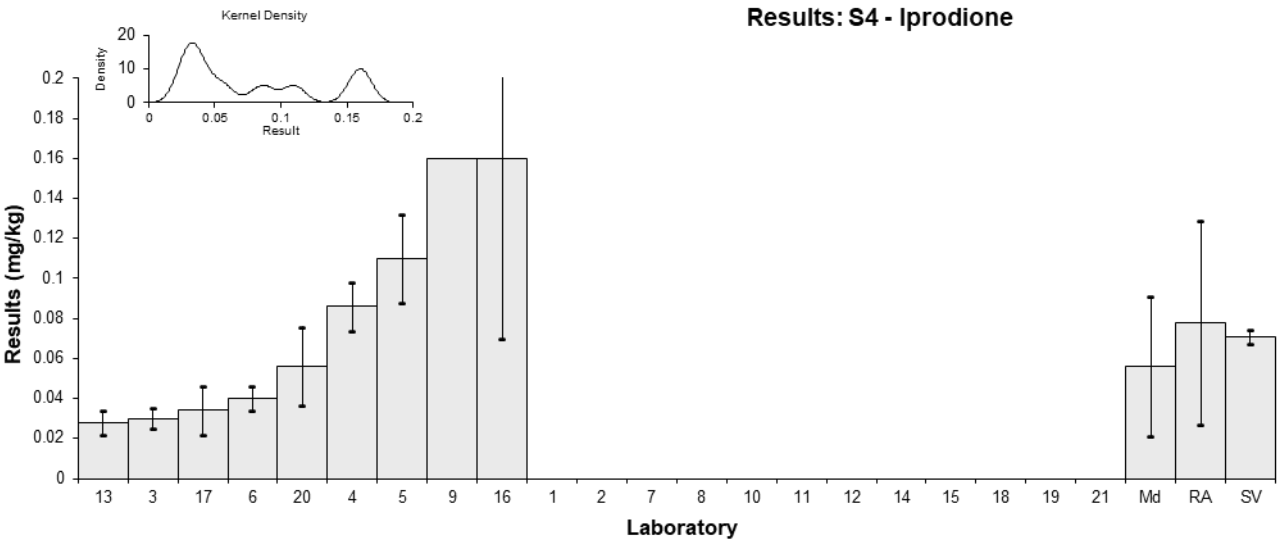

Results: S4 - Iprodione
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
13
3
17
6
20
4
5
9
16
1
2
7
8
10
11
12
14
15
18
19
21
Md
RA
SV

Figure 21

Table 25

Sample Details

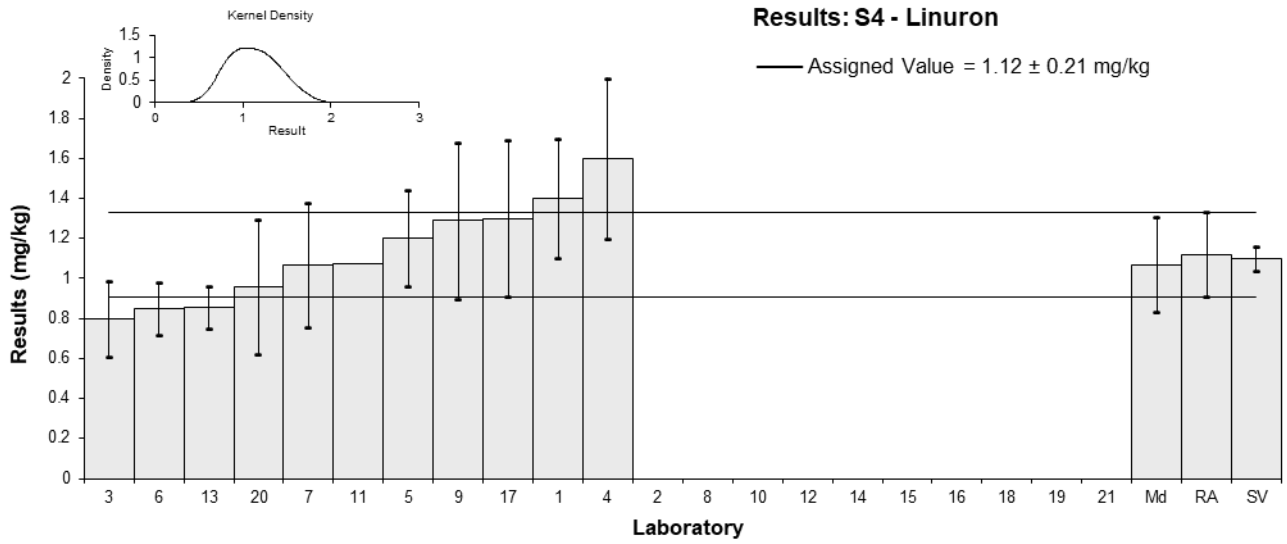
Sample No.	S4
Matrix	Coriander
Analyte	Linuron
Unit	mg/kg

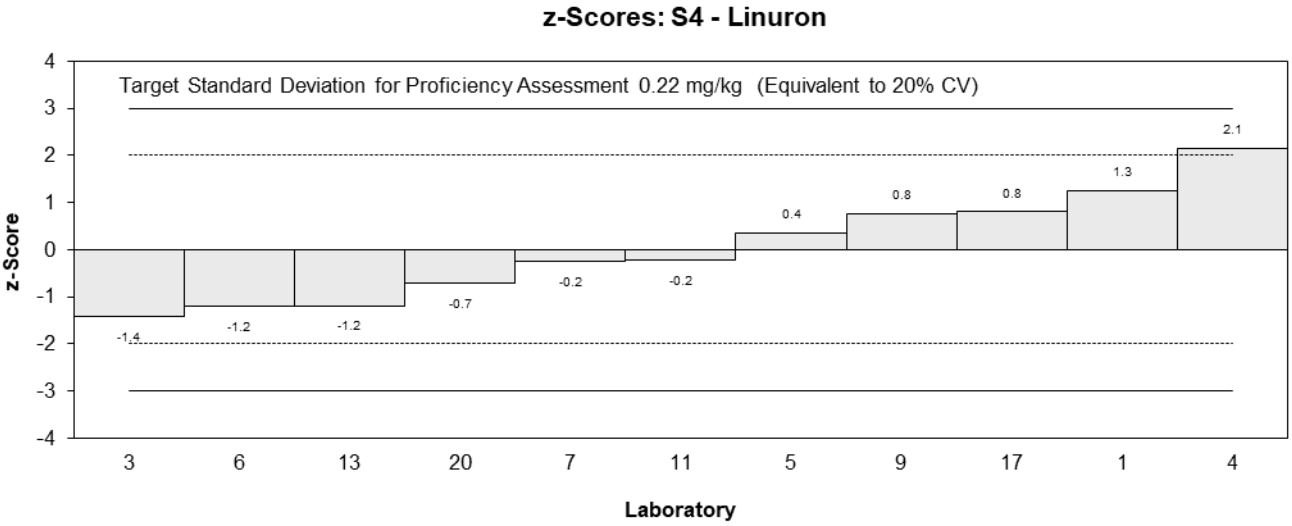
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	1.4	0.3	73	1.25	0.76
2	NT	NT	NT		
3	0.8	0.19	81	-1.43	-1.13
4	1.6	0.4	75	2.14	1.06
5	1.2	0.24	NR	0.36	0.25
6	0.85	0.13	91	-1.21	-1.09
7	1.0661	0.312	NR	-0.24	-0.14
8	NT	NT	NT		
9	1.29	0.39	71	0.76	0.38
10	NT	NT	NT		
11	1.071	NR	83	-0.22	-0.23
12	NT	NT	NT		
13	0.854	0.106	132.1	-1.19	-1.13
14	NT	NT	NT		
15	NT	NT	NT		
16	NT	NT	NT		
17	1.3	0.39	93	0.80	0.41
18	NT	NT	NT		
19	NT	NT	NT		
20	0.960	0.336	92	-0.71	-0.40
21	NT	NT	NT		

Statistics

Assigned Value	1.12	0.21
Spike Value	1.10	0.06
Robust Average	1.12	0.21
Median	1.07	0.24
Mean	1.13	
N	11	
Max	1.6	
Min	0.8	
Robust SD	0.28	
Robust CV	25%	


Kernel Density
Density
Result
Results: S4 - Linuron
Assigned Value = 1.12 ± 0.21 mg/kg
Results (mg/kg)
Laboratory
3 6 13 20 7 11 5 9 17 1 4 2 8 10 12 14 15 16 18 19 21 Md RA SV


z-Scores: S4 - Linuron
Target Standard Deviation for Proficiency Assessment 0.22 mg/kg (Equivalent to 20% CV)
z-Score
-1.4 -1.2 -1.2 -0.7 -0.2 -0.2 0.4 0.8 0.8 1.3 2.1
Laboratory
3 6 13 20 7 11 5 9 17 1 4

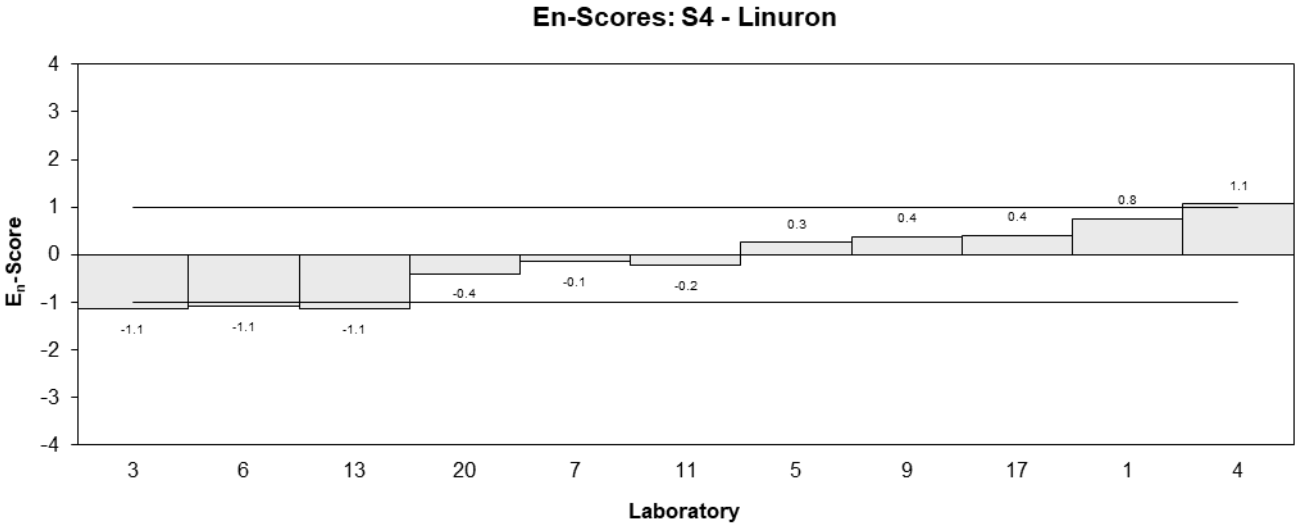

En-Scores: S4 - Linuron
En-Score
-1.1 -1.1 -1.1 -0.4 -0.1 -0.2 0.3 0.4 0.4 0.8 1.1
Laboratory
3 6 13 20 7 11 5 9 17 1 4

Figure 22

Table 26

Sample Details

Sample No.	S4
Matrix	Coriander
Analyte	Permethrin
Unit	mg/kg

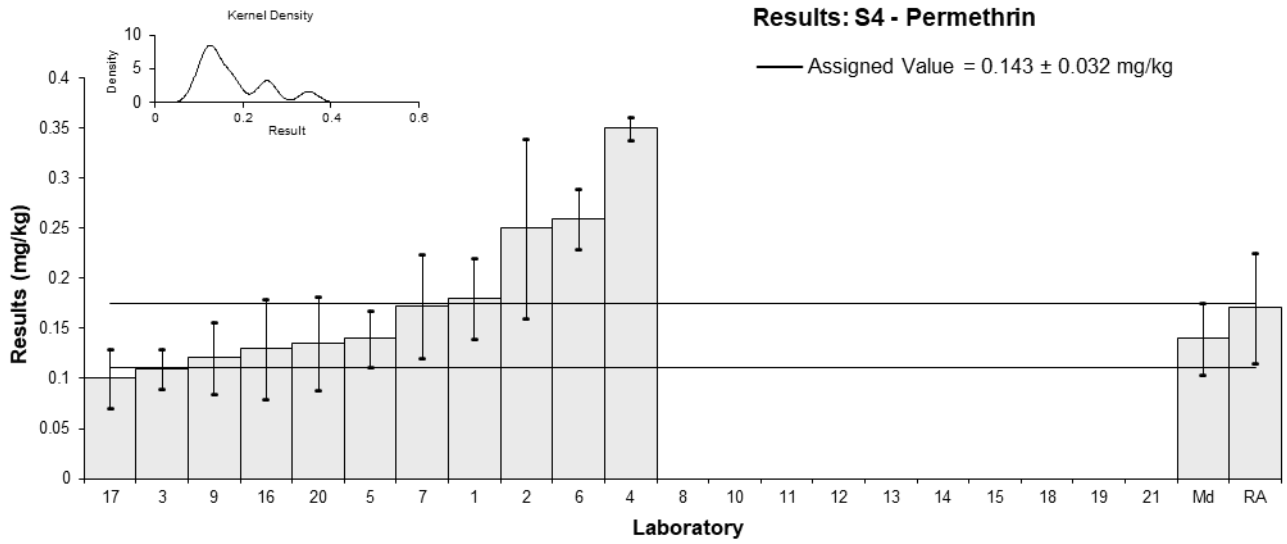
Participant Results

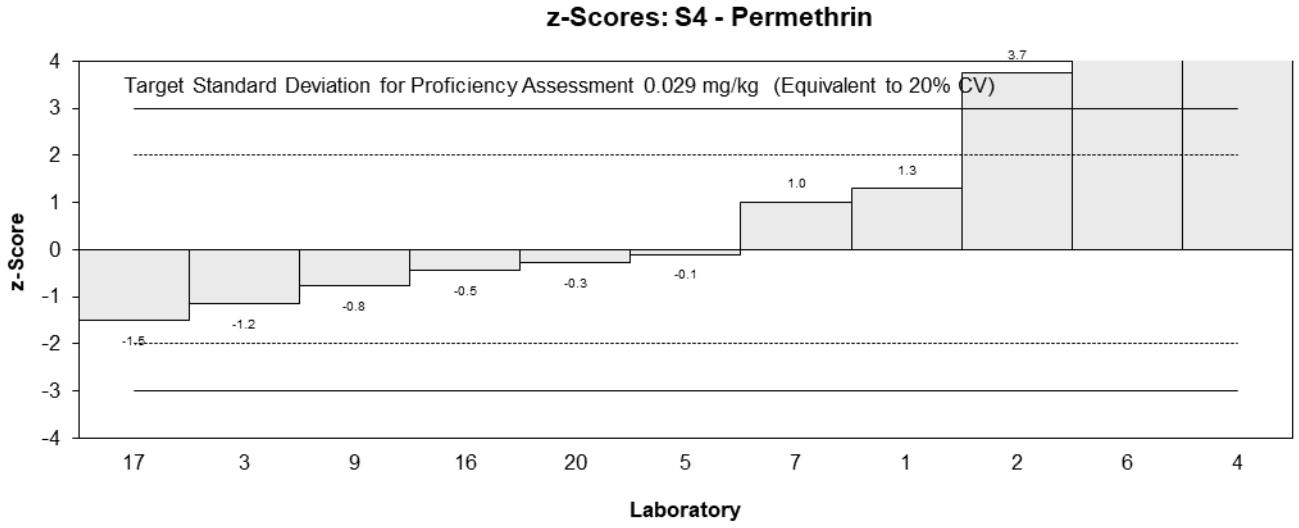
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.18	0.04	91	1.29	0.72
2	0.25	0.09	NR	3.74	1.12
3	0.11	0.02	86	-1.15	-0.87
4*	0.35	0.012	NR	7.24	6.06
5	0.14	0.028	NR	-0.10	-0.07
6*	0.26	0.03	114	4.09	2.67
7	0.172	0.052	NR	1.01	0.47
8	NT	NT	NT		
9	0.121	0.036	100	-0.77	-0.46
10	NR	NR	NR		
11	NT	NT	NT		
12	NT	NT	NT		
13	NT	NT	NT		
14	NT	NT	NT		
15	NT	NT	NT		
16	0.13	0.05	NR	-0.45	-0.22
17	0.10	0.03	69	-1.50	-0.98
18	<0.01	NR	170		
19	NR	NR	NR		
20	0.135	0.047	103	-0.28	-0.14
21	<0.01	NR	192		

* Outlier, see Section 4.2

Statistics

Assigned Value	0.143	0.032
Spike Value	Not Spiked	
Robust Average	0.171	0.055
Median	0.140	0.036
Mean	0.177	
N	11	
Max	0.35	
Min	0.1	
Robust SD	0.073	
Robust CV	43%	


Results: S4 - Permethrin
Assigned Value = 0.143 ± 0.032 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
17 3 9 16 20 5 7 1 2 6 4 8 10 11 12 13 14 15 18 19 21 Md RA


z-Scores: S4 - Permethrin
Target Standard Deviation for Proficiency Assessment 0.029 mg/kg (Equivalent to 20% CV)
z-Score
Laboratory
17 3 9 16 20 5 7 1 2 6 4
-1.5 -1.2 -0.8 -0.5 -0.3 -0.1 1.0 1.3 3.7

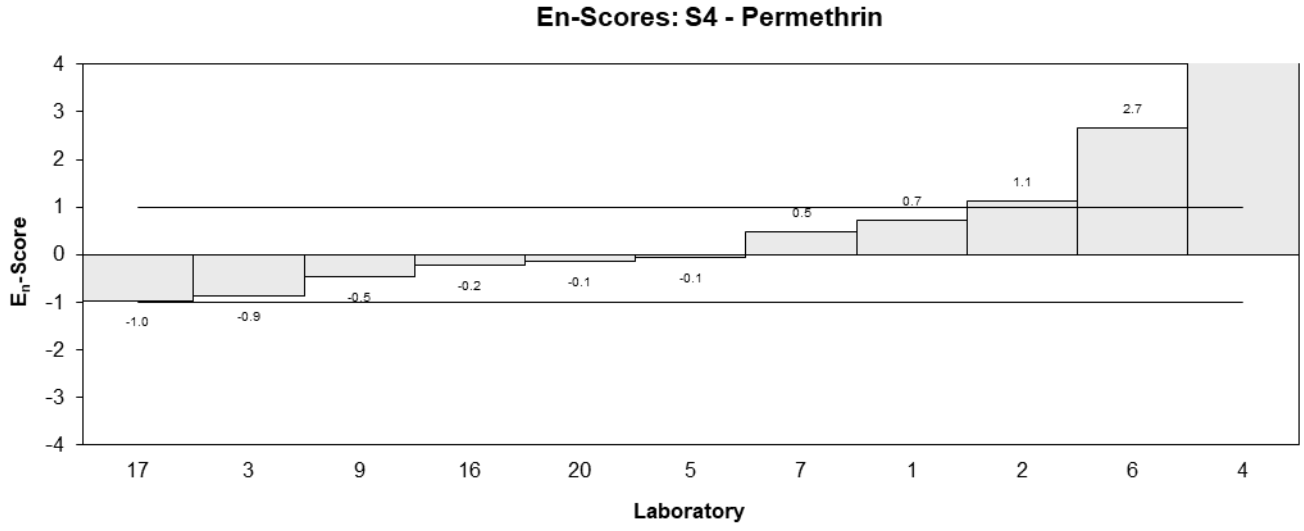

En-Scores: S4 - Permethrin
En-Score
Laboratory
17 3 9 16 20 5 7 1 2 6 4
-1.0 -0.9 -0.5 -0.2 -0.1 -0.1 0.5 0.7 1.1 2.7

Figure 23

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The robust averages and associated expanded uncertainties were calculated using the procedure described in ISO 13528.[7] The assigned values for all scored analytes were the robust averages of participants' results, after results less than 50% and greater than 150% of the robust average had been removed.[3,4] The calculation of the expanded uncertainty for a robust average is presented in Appendix 3.

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

No assigned value was set for Sample S1 chlorothalonil as there was very poor recovery compared to the spiked value. No assigned value was set for Sample S2 iprodione, Sample S3 metrafenone, and Sample S4 cypermethrin and iprodione due to the high variability of participants' results. These issues may have been due to the matrix, mass fraction level, properties of the analyte itself, or a combination of these factors. For these analytes, participants may still compare their results with the descriptive statistics and spiked value, if applicable, as presented in Section 5.

For all analytes spiked into the samples, a comparison of the assigned value (or robust average if no assigned value was set) and the spiked value is presented in Table 27. Assigned values were between 81% and 102% of the spiked values, providing good support for the assigned values and evidence for the stability of these analytes in the test samples.

Table 27 Comparison of Assigned Values *(Robust Averages)* and Spiked Values

Sample	Analyte	Assigned Value *(Robust Average)* (mg/kg)	Spiked Value (mg/kg)	Assigned Value *(Robust Average)* / Spiked Value (%)
S1	Chlorothalonil	*(0.37)*	0.998	*(37)*
	Chlorpyrifos	0.732	0.821	89
	Endosulfan sulfate	0.426	0.447	95
	Fenhexamid	0.464	0.502	92
S2	Bifenthrin	0.0158	0.0167	95
	Indoxacarb	2.68	3.01	89
	Iprodione	*(5.4)*	8.04	*(67)*
S3	Acetamiprid	0.184	0.181	102
	Cyprodinil	1.61	1.83	88
	Metrafenone	*(0.77)*	1.10	*(70)*
S4	Fipronil	0.068	0.0835	81
	Iprodione	*(0.078)*	0.0706	*(110)*
	Linuron	1.12	1.10	102

6.2 Measurement Uncertainty Reported by Participants

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

Laboratory **11** did not report any uncertainties; this participant reported that they were accredited to ISO/IEC 17025. Laboratories **4**, **9**, **10** and **14** reported uncertainties for only some of their reported numeric results; Laboratory **9** was not accredited, however the other participants reported that they were accredited to ISO/IEC 17025.

The magnitude of the reported uncertainties for spiked analytes in this study was within the range 3.4% to 250000% relative to the result. In general, an expanded uncertainty of less than 15% relative may be unrealistically small for the routine measurement of a pesticide residue, while over 50% may be too large and not fit for purpose. Of the 244 expanded uncertainties, 28 were less than 15% relative and 23 were greater than 50% relative.

For this PT study, participants were requested to report absolute expanded uncertainties in units of mg/kg. Laboratory **9** reported all uncertainties as relative uncertainties (i.e. uncertainties were reported as '*x*%'); these values were modified accordingly for this report by the study coordinator. Laboratory **15** reported all uncertainties as '50', resulting in very large relative uncertainties across all results. It is likely that this participant's uncertainties were intended to be relative uncertainties, however, there was no clear indication that this was the case, and therefore no modifications of these uncertainties were made for this report. Laboratory **8** reported one result with a relative uncertainty of 317%. Laboratory **12** reported three results with a relative uncertainty of 200% and a further two results with a relative uncertainty of 100%. In general, participants should ensure that they have reported their uncertainties with the correct units as requested by the client.

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

In some cases the results were reported with an inappropriate number of significant figures. Including too many significant figures may inaccurately reflect the precision of measurements. The recommended format is to write the uncertainty to no more than two significant figures, and then to write the result with the corresponding number of decimal places. For example, instead of 0.4701 ± 0.184 mg/kg, it is recommended to report 0.47 ± 0.18 mg/kg.[10]

6.3 *z*-Scores

Target SDs equivalent to 15% PCV were used to calculate *z*-scores for spiked analytes in Samples S1, S2 and S3. Target SDs equivalent to 20% PCV were used to calculate z-scores for incurred analytes in Samples S3 as there were no spiked values available for comparison, and for all analytes in Sample S4 as coriander was a new matrix introduced in this PT study. CVs predicted by the Thompson-Horwitz equation,[8] between-laboratory CVs obtained in this study, and target SDs (as PCV) are presented for comparison in Table 28.

Table 28 Comparison of Thompson-Horwitz CVs, Target SDs, and Between-Laboratory CV

Sample	Analyte	Assigned Value *(Robust Average)* (mg/kg)	Thompson-Horwitz CV[a] (%)	Between-Laboratory CV[b] (%)	Target SD (as PCV) (%)
S1	Chlorothalonil	*(0.37)*	*(19)*	39	Not Set
	Chlorpyrifos	0.732	17	16	15
	Endosulfan sulfate	0.426	18	26	15
	Fenhexamid	0.464	18	23	15
S2	Bifenthrin	0.0158	22	26	15

Sample	Analyte	Assigned Value *(Robust Average)* (mg/kg)	Thompson-Horwitz CV[a] (%)	Between-Laboratory CV[b] (%)	Target SD (as PCV) (%)
	Indoxacarb	2.68	14	19	15
	Iprodione	*(5.4)*	*(12)*	53	Not Set
S3	Acetamiprid	0.184	21	14	15
	Bifenthrin	0.0199	22	24	20
	Chlorpyrifos	0.0328	22	22	20
	Cyprodinil	1.61	15	26	15
	Fenhexamid	0.0274	22	20	20
	Metalaxyl	0.058	22	29	20
	Methomyl	0.0355	22	14	20
	Metrafenone	*(0.77)*	*(17)*	53	Not Set
S4	Chlorpyrifos	0.0187	22	36	20
	Cypermethrin	*(0.076)*	*(22)*	76	Not Set
	Cyprodinil	0.0219	22	33	20
	Fipronil	0.068	22	25	20
	Iprodione	*(0.078)*	*(22)*	78	Not Set
	Linuron	1.12	16	25	20
	Permethrin	0.143	21	27	20

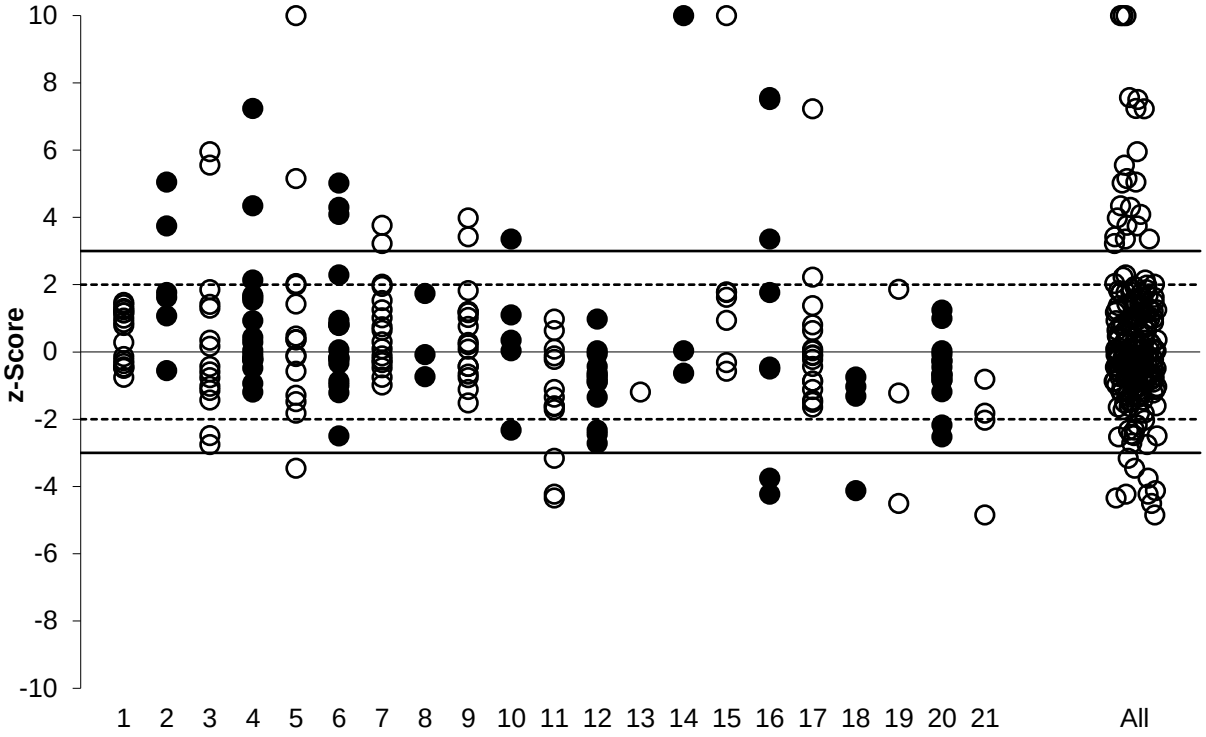
[a] Calculated from the assigned value (robust average).

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

Of 217 results for which *z*-scores were calculated, 171 (79%) returned $|z| \leq 2.0$, indicating a satisfactory performance.

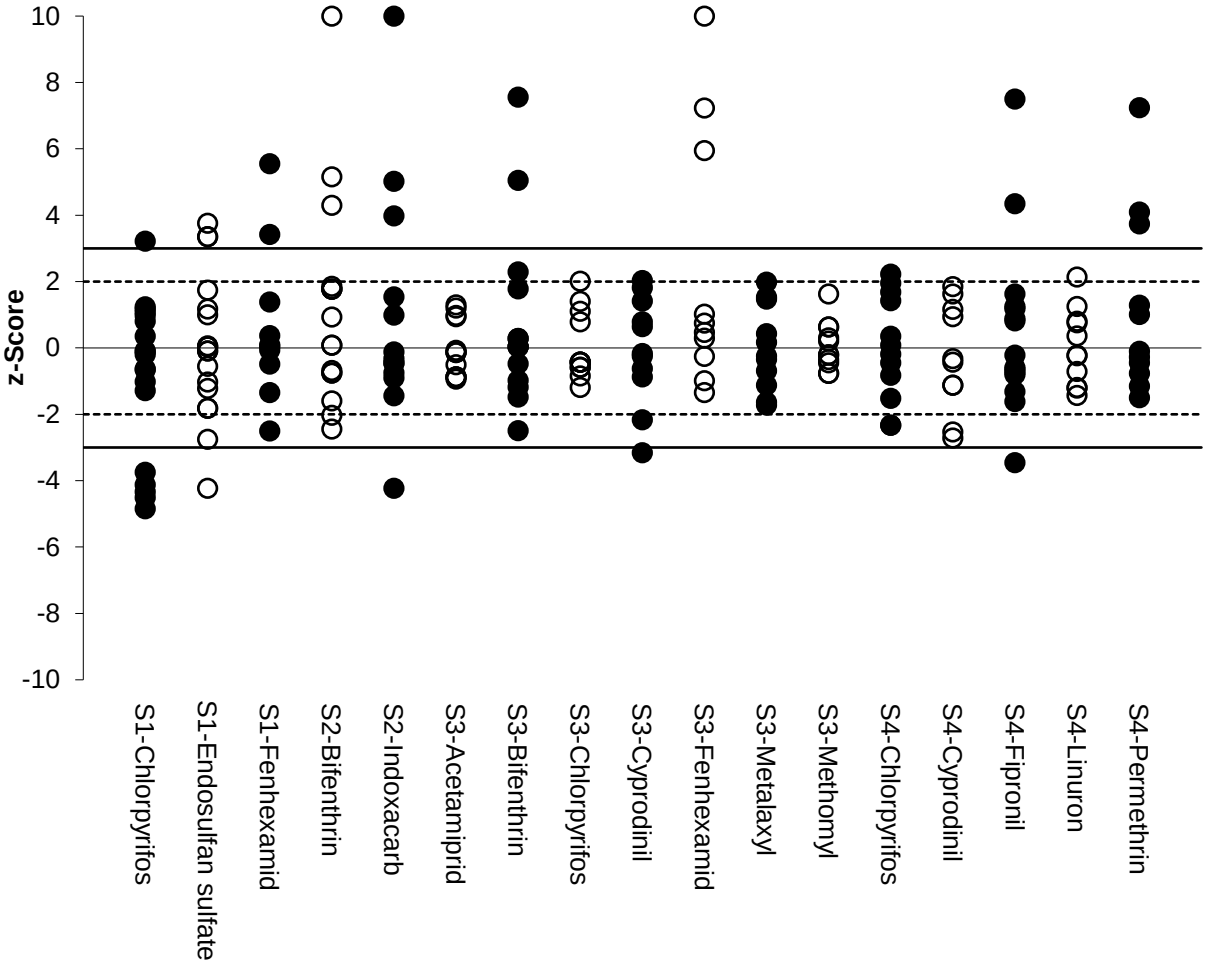
Laboratories **1**, **4**, **6**, **7**, **9** and **17** reported numeric results for all 17 scored analytes. Laboratory **1** achieved satisfactory *z*-scores for all analytes. Two other participants received satisfactory *z*-scores for all scored analytes that they reported results for: **8** (3) and **13** (1).

The dispersal of participants' *z*-scores is presented graphically by laboratory in Figure 24 and by analyte in Figure 25.



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

Figure 24 *z*-Score Dispersal by Laboratory



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

Figure 25 *z*-Score Dispersal by Analyte

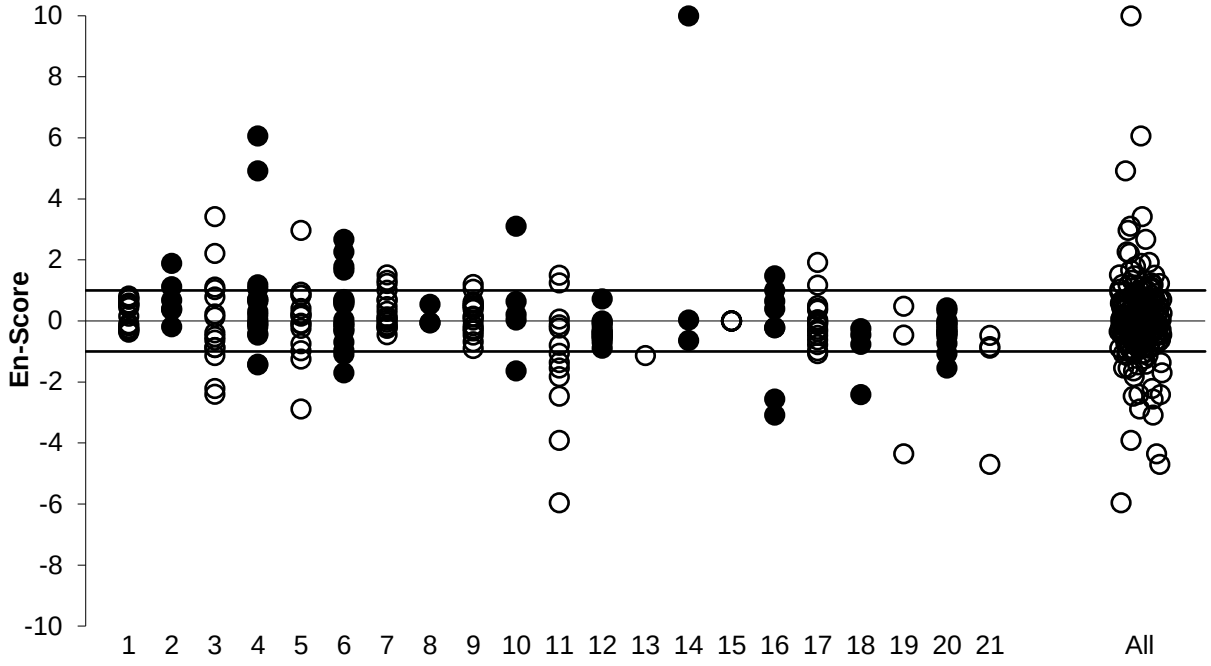
6.4 E_n-Scores

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

Of 217 results for which E_n-scores were calculated, 162 (75%) returned $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratory **1** achieved satisfactory E_n-scores for all 17 scored analytes in this study. Two other participants received satisfactory E_n-scores for all scored analytes that they reported results for: **12** (13) and **8** (3). Laboratory **15** also returned satisfactory E_n-scores for all scored analytes reported, however their uncertainties were all greater than 600% relative, which was not fit for purpose.

The dispersal of participants' E_n-scores is presented graphically by laboratory in Figure 26.



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

Figure 26 E_n-Score Dispersal by Laboratory

6.5 Range of Pesticides Analysed by Participants

Participants were provided with a list of potential analytes that the samples could be analysed for (Table 1). Of these, 16 different analytes were assessed in this study, with five analytes being in multiple samples. Participants were not required to test for all analytes, and were requested to report 'NT' (for 'Not Tested') for pesticides they did not test for. A summary of participants' testing of the pesticides in this study is presented in Table 29 (participants have only been recorded as 'NT' if they reported 'NT' for that analyte across all samples).

Laboratories **1**, **5**, **6**, **9**, **11** and **17** reported that they tested for all analytes assessed in this study. The proportion of analytes each participant tested for ranged from 19% to 100%.

Of the analytes in this study, the highest proportion of participants (95%) tested for chlorpyrifos. The proportion of participants testing for each analyte in this study ranged from 43% to 95%.

Table 29 Summary of Pesticides Analysed by Participants

Analyte \ Lab. Code	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	Proportion of Participants (%)
Acetamiprid	✓	NT	✓	✓	✓	✓	✓	NT	✓	NT	✓	✓	NT	NT	✓	✓	✓	NT	NT	✓	NT	62
Bifenthrin	✓	✓	✓	✓	✓	✓	✓	NT	✓	✓	✓	✓	NT	✓	✓	✓	✓	✓	✓	✓	✓	90
Chlorothalonil	✓	NT	✓	✓	✓	✓	✓	NT	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	NT	NT	NT	71
Chlorpyrifos	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	✓	✓	✓	✓	✓	✓	✓	✓	95
Cypermethrin	✓	✓	✓	✓	✓	✓	✓	NT	✓	✓	✓	✓	NT	✓	✓	✓	✓	✓	✓	✓	✓	90
Cyprodinil	✓	NT	✓	✓	✓	✓	✓	NT	✓	NT	✓	✓	NT	NT	NT	NT	✓	NT	NT	✓	NT	52
Endosulfan sulfate	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	NT	✓	✓	✓	✓	✓	✓	✓	✓	90
Fenhexamid	✓	NT	✓	✓	✓	✓	✓	NT	✓	NT	✓	✓	NT	NT	✓	NT	✓	NT	NT	NT	NT	52
Fipronil	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	✓	NT	NT	NT	✓	✓	✓	✓	✓	✓	✓	81
Indoxacarb	✓	NT	NT	✓	✓	✓	✓	NT	✓	NT	✓	✓	NT	NT	✓	✓	✓	✓	NT	✓	NT	62
Iprodione	✓	✓	✓	✓	✓	✓	NT	NT	✓	NT	✓	✓	✓	NT	✓	✓	✓	✓	NT	✓	NT	71
Linuron	✓	NT	✓	✓	✓	✓	✓	NT	✓	NT	✓	NT	✓	NT	✓	NT	✓	NT	NT	✓	NT	57
Metalaxyl	✓	NT	✓	✓	✓	✓	✓	NT	✓	NT	✓	✓	NT	NT	✓	NT	✓	NT	✓	✓	NT	62
Methomyl	✓	NT	✓	✓	✓	✓	✓	NT	✓	NT	✓	✓	NT	NT	✓	NT	✓	NT	NT	✓	NT	57
Metrafenone	✓	NT	NT	NT	✓	✓	NT	NT	✓	NT	✓	✓	NT	NT	✓	NT	✓	NT	NT	✓	NT	43
Permethrin	✓	✓	✓	✓	✓	✓	✓	NT	✓	✓	✓	NT	NT	NT	✓	✓	✓	✓	✓	✓	✓	81
Proportion of Analytes (%)	100	44	88	94	100	100	88	19	100	38	100	75	19	31	94	63	100	50	44	88	38	

6.6 False Negatives

Table 30 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 30 False Negatives

Lab. Code	Sample	Analyte	Assigned Value *(Robust Average)* (mg/kg)	Spiked Value (mg/kg)	Result[a] (mg/kg)
1	S4	Iprodione	*(0.078)*	0.0706	NR
2	S3	Chlorpyrifos	0.0328	Not Spiked	NR
	S4	Chlorpyrifos	0.0187	Not Spiked	NR
		Iprodione	*(0.078)*	0.0706	NR
3	S2	Bifenthrin	0.0158	0.0167	NR
5	S3	Methomyl	0.0355	Not Spiked	NR
	S4	Cyprodinil	0.0219	Not Spiked	NR
10	S2	Bifenthrin	0.0158	0.0167	NR
	S4	Permethrin	0.143	Not Spiked	NR
11	S2	Iprodione	*(5.4)*	8.04	<0.02
	S3	Chlorpyrifos	0.0328	Not Spiked	<0.02
		Fenhexamid	0.0274	Not Spiked	<0.02
	S4	Iprodione	*(0.078)*	0.0706	<0.02
14	S3	Bifenthrin	0.0199	Not Spiked	NR
		Chlorpyrifos	0.0328	Not Spiked	NR
	S4	Chlorpyrifos	0.0187	Not Spiked	NR
16	S1	Chlorothalonil	*(0.37)*	0.998	NR
	S3	Chlorpyrifos	0.0328	Not Spiked	NR
	S4	Chlorpyrifos	0.0187	Not Spiked	NR
18	S2	Bifenthrin	0.0158	0.0167	<0.01
	S3	Bifenthrin	0.0199	Not Spiked	<0.01
		Chlorpyrifos	0.0328	Not Spiked	<0.01
	S4	Chlorpyrifos	0.0187	Not Spiked	<0.01
		Iprodione	*(0.078)*	0.0706	<0.01
		Permethrin	0.143	Not Spiked	<0.01
19[b]	S3	Bifenthrin	0.0199	Not Spiked	NR
		Chlorpyrifos	0.0328	Not Spiked	NR
		Metalaxyl	0.058	Not Spiked	NR
	S4	Chlorpyrifos	0.0187	Not Spiked	NR
		Fipronil	0.068	0.0835	NR
		Permethrin	0.143	Not Spiked	NR
21	S3	Bifenthrin	0.0199	Not Spiked	<0.01
		Chlorpyrifos	0.0328	Not Spiked	<0.01
	S4	Chlorpyrifos	0.0187	Not Spiked	<0.01
		Permethrin	0.143	Not Spiked	<0.01

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

[b] Participants were instructed to not correct results for any pesticide found in the unspiked sample. After the release of the interim report, Laboratory **19** reported that they had detected incurred analytes in Samples S3 and S4, however did not report numeric results for these analytes.

6.7 Reporting of Non-Spiked Analytes

For this study, samples were prepared from organic matrices (Samples S1 and S2), as well as matrices with incurred analytes (Samples S3 and S4). Incurred analytes in Samples S3 and S4 where at least ten participants reported numeric results were assessed in this PT study. Other pesticides which were not spiked into the test samples by the study coordinator are presented in Table 31 for information only, ordered by sample and analyte.

Table 31 Non-Spiked Analytes Reported by Participants

Sample	Analyte	Lab. Code	Spiked Sample Result (mg/kg)	Spiked Sample Uncertainty (mg/kg)	Spiked Sample Recovery (%)	Unspiked Sample Result (mg/kg)
S2	Chlorothalonil	14	1.056	NR	101.44	NR*
S3	Clothianidin	15	0.017	50	147	Detected
	Fludioxonil	1	0.028	0.008	91	NR
		3	0.02	0.003	93	NR
		4	0.026	NR	114	Detected
		5	0.027	0.014	NR	Detected
		6	0.025	0.003	99	0.025
		7	0.029	0.012	NR	0.02
		9	0.026	0.008	83	0.024
		15	0.016	50	108	Detected
		17	0.025	0.0075	76	NR
	Prothiofos	1	0.0033	0.009	93	Detected
		4	0.028	0.004	111	Detected
		6	0.036	NR	79	0.036
		7	0.026	0.0065	NR	0.03
		15	0.024	NR	NR	NR
	Pyrimethanil	1	0.0093	0.003	89	Detected
S4	2,4-D	7	0.2323	0.07	NR	NR
	Azoxystrobin	1	0.01	0.004	90	Detected
		3	0.01	0.001	103	NR
		5	0.012	0.006	NR	NR
		6	0.012	0.002	106	0.012
		17	0.007	0.0021	106	NR
	Fenvalerate	2	0.13	0.06	NR	Detected
	Fludioxonil	1	0.007	0.003	NR	Detected
		17	0.012	0.0036	104	NR
	Imidacloprid	1	0.007	0.003	NR	Detected
		5	0.012	0.006	NR	Detected
		17	0.0055	0.0017	103	NR
	Metalaxyl	3	0.01	0.001	104	NR

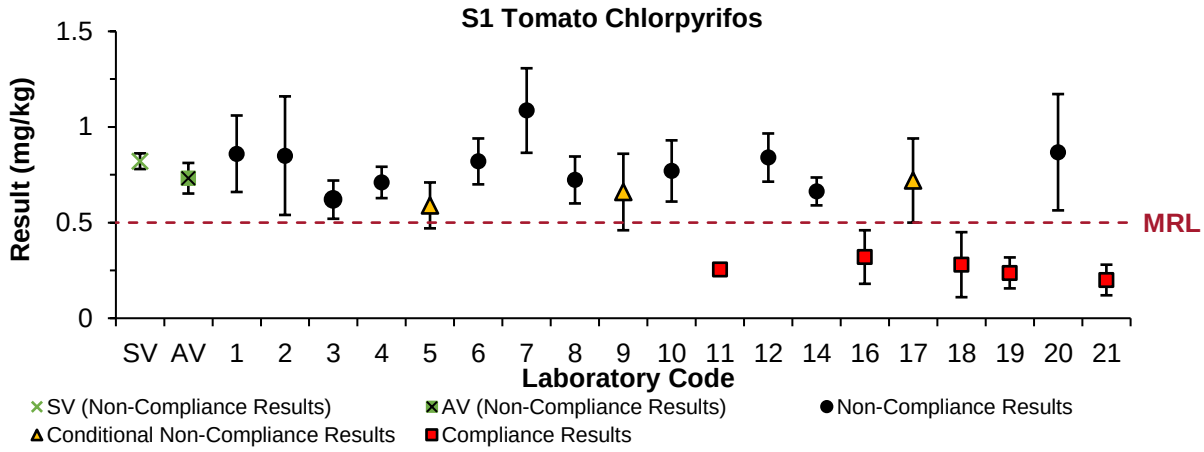
* Sample S2 was prepared using organic bok choy, and did not contain any incurred analytes.

6.8 Fitness for Purpose of Pesticide Results

Internationally, there are several standards that set MRLs for various pesticides in different food products, typically to ensure that these products will not cause any adverse health effects when consumed. One standard that sets MRLs to food products in Australia is the Australia New Zealand Food Standards Code.[5] Laboratories need to ensure accurate measurements of these food products, so that their result correctly reflects whether a sample is compliant with the relevant MRL. For this study, eleven analytes were spiked into the samples to be at either above (non-compliant) or below (compliant) the associated Australia New Zealand Food Standards Code MRL. Of these analytes, seven had assigned values (Sample S1 chlorpyrifos and fenhexamid, Sample S2 bifenthrin and indoxacarb, Sample S3 acetamiprid and cyprodinil, and Sample S4 linuron), and all of these analytes' assigned values matched the spiked values in regard to compliance or non-compliance with the MRL.

Figures 27 to 33 show comparisons of the spiked value (SV), assigned values (AV), participants' results, and MRLs for these seven assessed analytes. Only numeric results have been included. In some cases, the MRL refers to the sum of a number of different permitted residues,[5] and not only the named analyte given here.

For the seven analytes considered, most participants' results correctly reflected compliance or non-compliance. Of 93 results assessed, 72 (77%) gave the correct compliance status inclusive of uncertainty, and 14 (15%) gave conditionally correct compliance statuses (i.e. the result gave the correct compliance status but the uncertainty spanned the MRL). Laboratory **4** returned the correct compliance status, and Laboratories **1**, **6**, **7**, **9** and **17** returned either the correct or conditionally correct compliance statuses, for all assessed analytes.



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

Figure 27 Sample S1 Tomato Chlorpyrifos Spiked and Assigned Value, Results and MRL

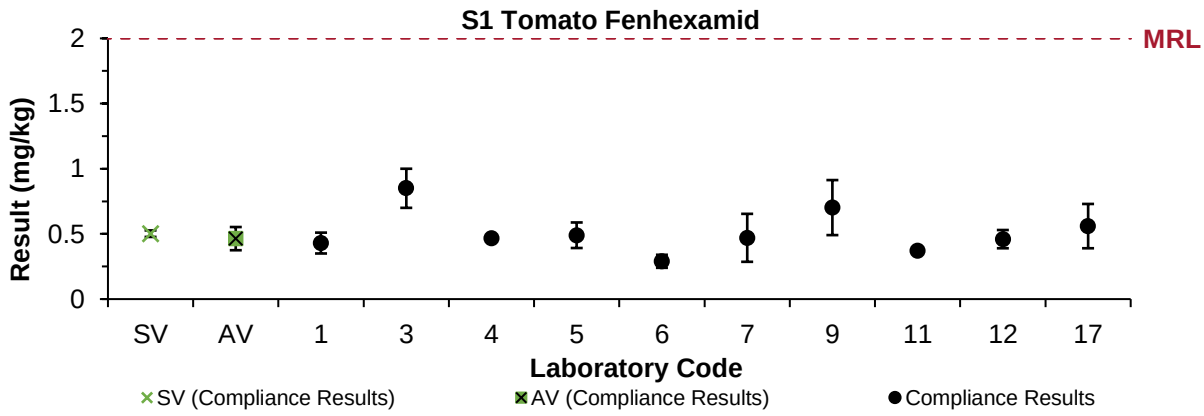
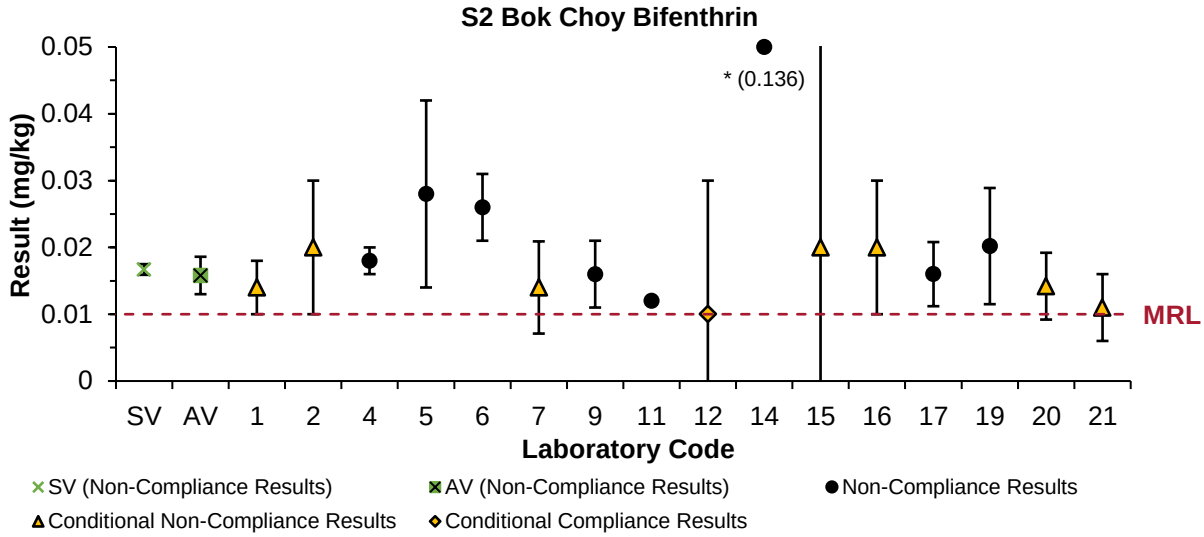
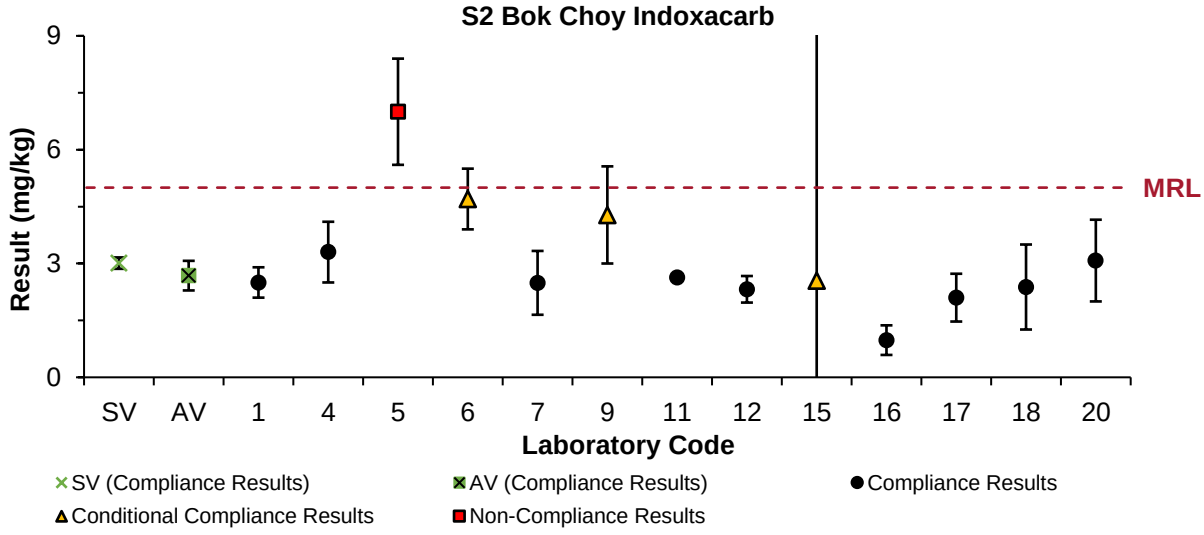


Figure 28 Sample S1 Tomato Fenhexamid Spiked and Assigned Value, Results and MRL



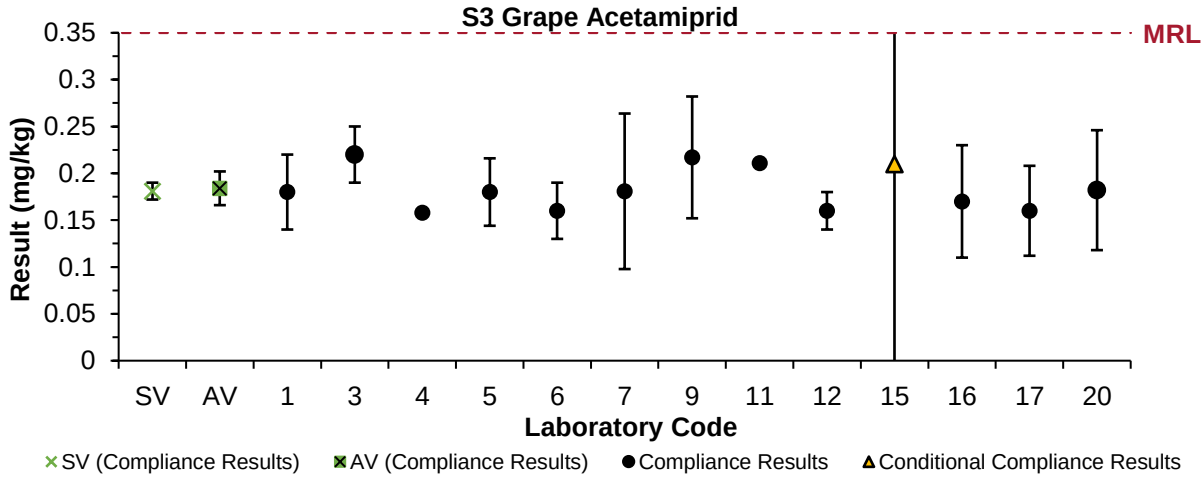
* Laboratory 14 result and uncertainty have been scaled to fit on the chart; original result in brackets.
The sample was non-compliant with the MRL, therefore participants with compliance results are in breach.

Figure 29 Sample S2 Bok Choy Bifenthrin Spiked and Assigned Value, Results and MRL



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

Figure 30 Sample S2 Bok Choy Indoxacarb Spiked and Assigned Value, Results and MRL



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

Figure 31 Sample S3 Grape Acetamiprid Spiked and Assigned Value, Results and MRL

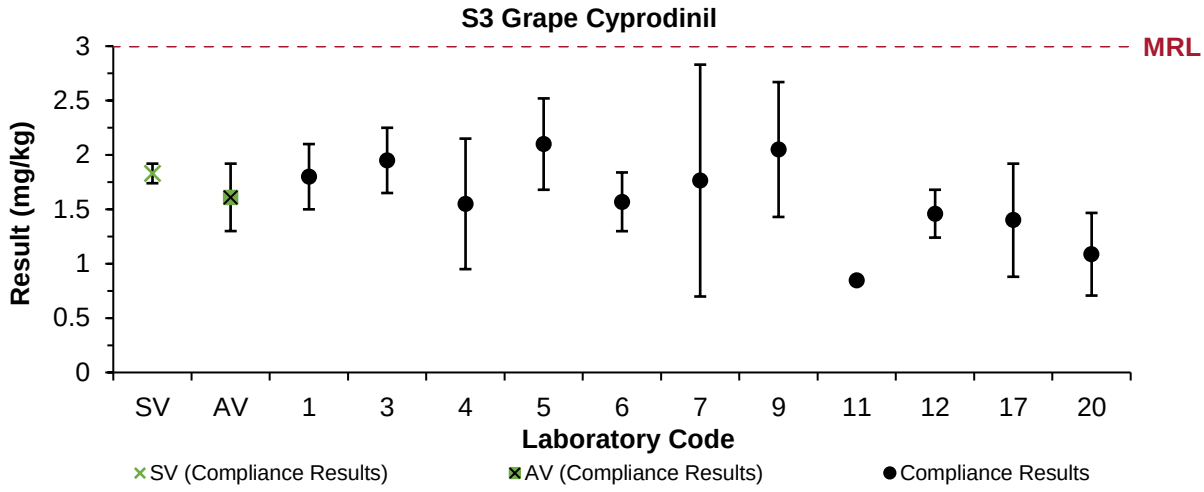


Figure 32 Sample S3 Grape Cyprodinil Spiked and Assigned Value, Results and MRL

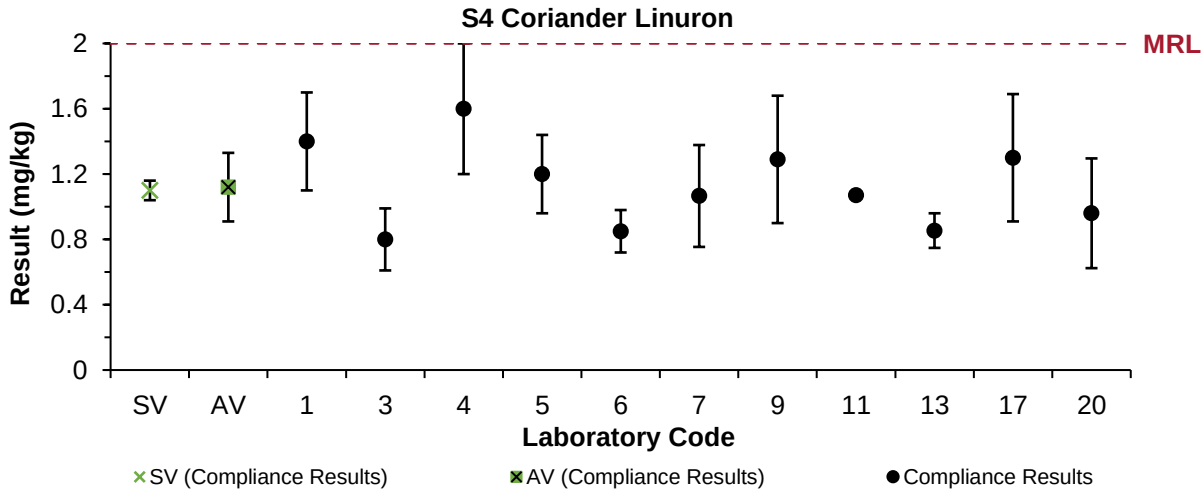
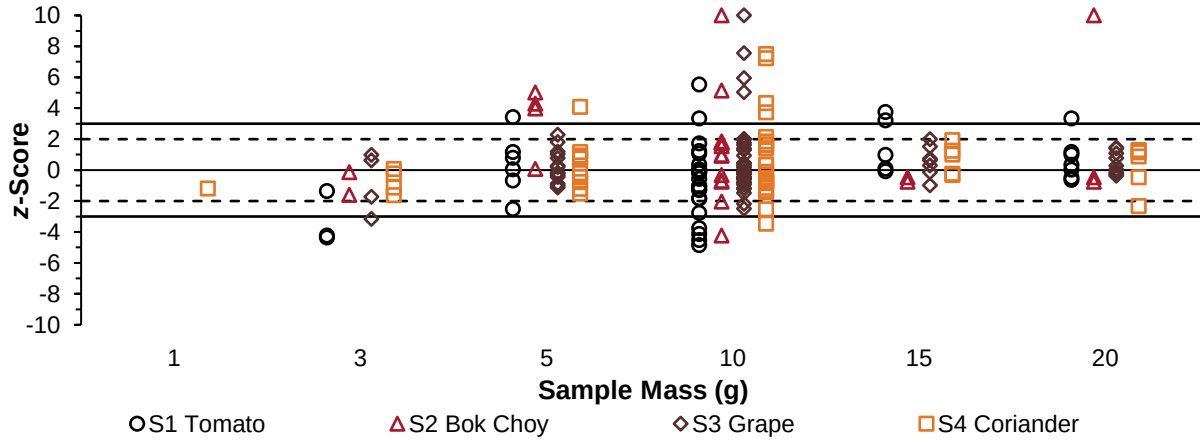


Figure 33 Sample S4 Coriander Linuron Spiked and Assigned Value, Results and MRL

6.9 Participants' Analytical Methods

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

Figure 34 shows *z*-scores obtained compared to the sample masses used for analysis. Participants reported using sample sizes between 1 g and 20 g per analysis, with most participants using 10 g.



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

Figure 34 *z*-Score vs Sample Mass Used for Analysis

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

Results compared to methodology used for all scored analytes are presented in Figures 35 to 51; participant's results yielding unsatisfactory *z*-scores ($|z| \geq 3.0$) have been circled for reference. Participants used a wide variety of methodologies, and there was no significant trend observed between results obtained and methodology used. The most common methodology was extraction using the QuEChERS procedure,[12] with ACN as the extraction solvent and using GC-MS/MS or LC-MS/MS for analysis.

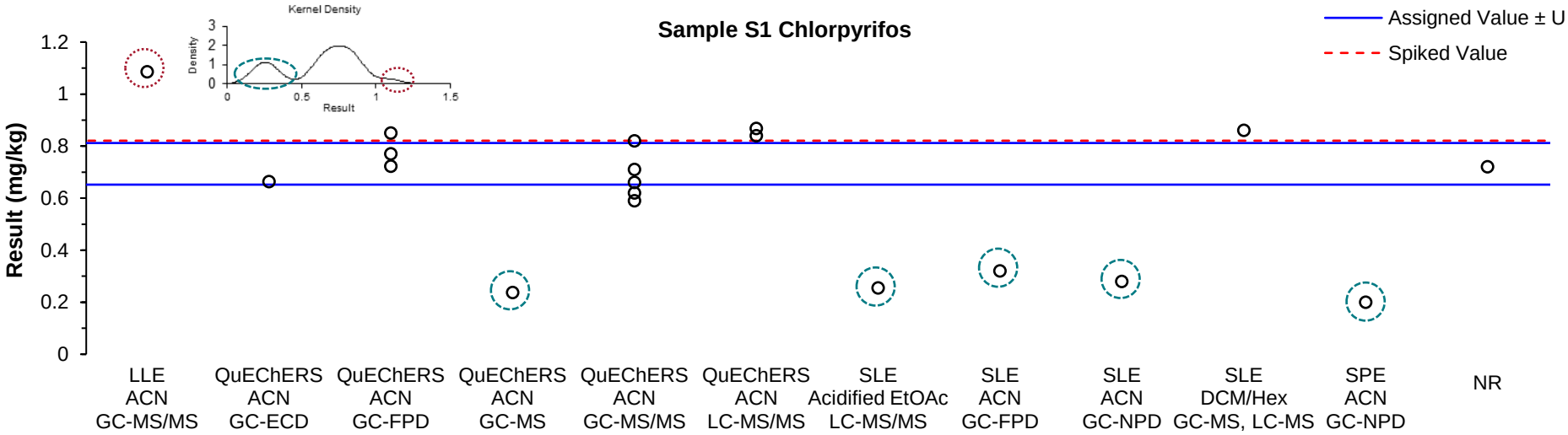


Figure 35 Sample S1 Tomato Chlorpyrifos Result vs Methodology

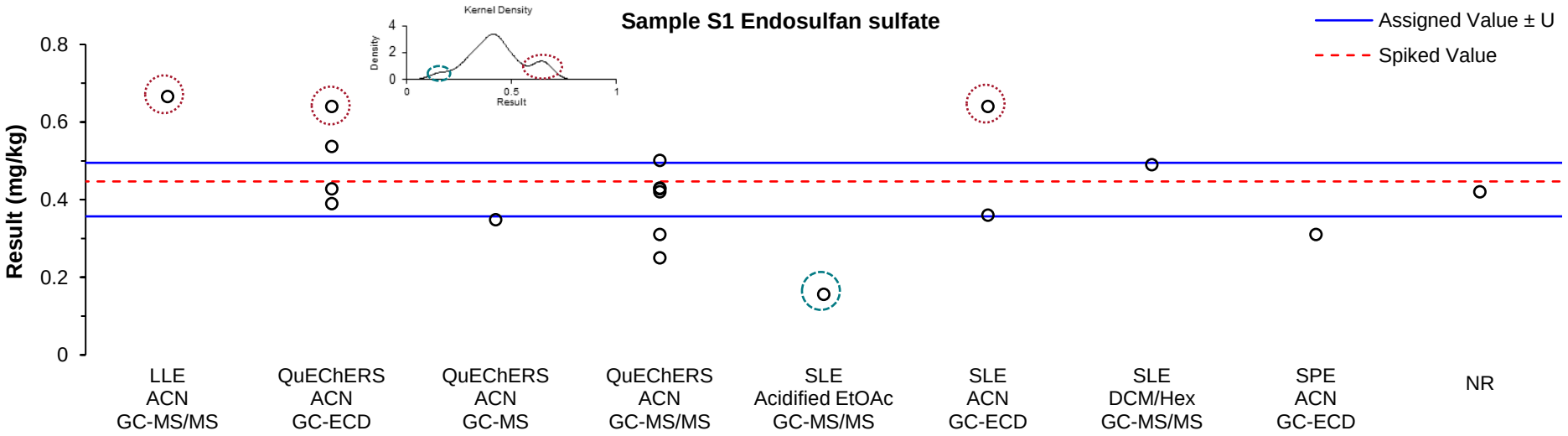


Figure 36 Sample S1 Tomato Endosulfan Sulfate Result vs Methodology

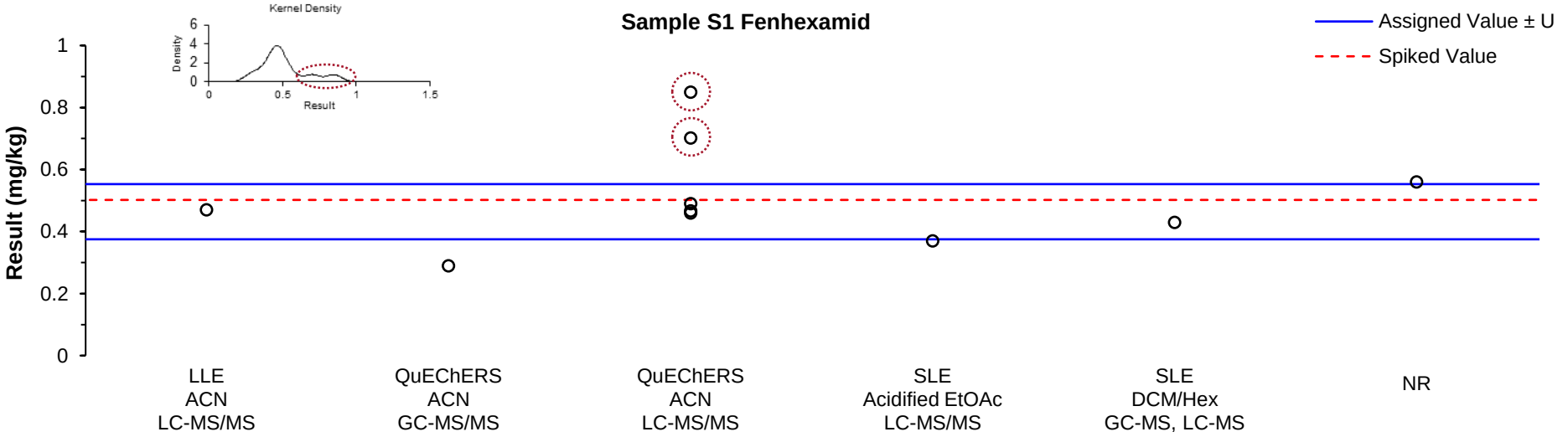
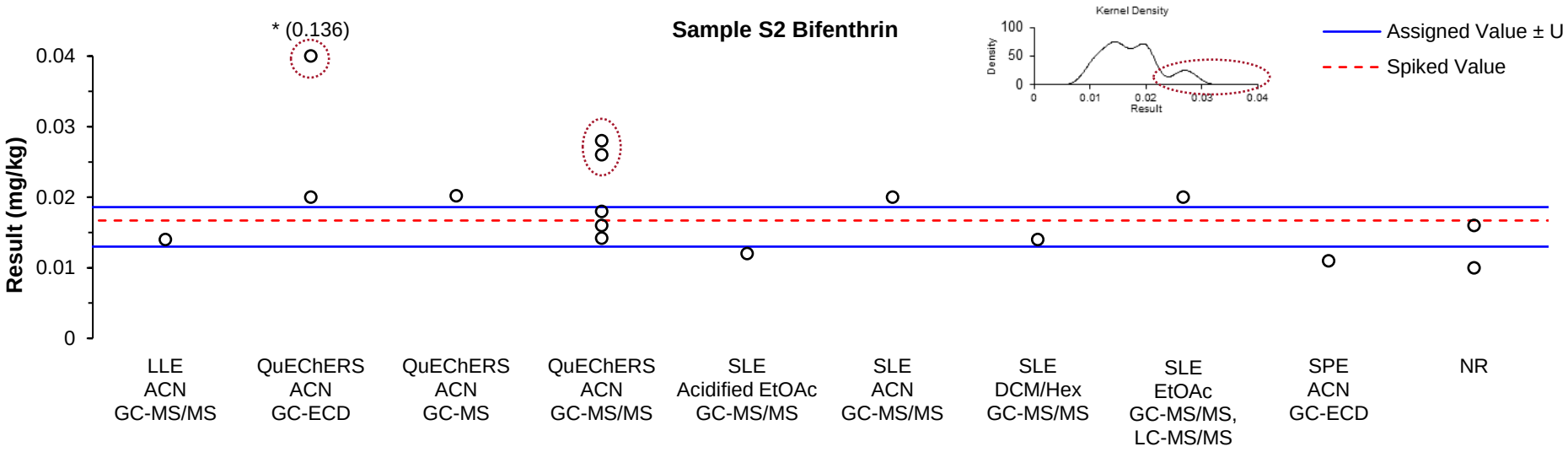


Figure 37 Sample S1 Tomato Fenhexamid Result vs Methodology



* Result has been scaled to fit on graph; actual result in brackets.

Figure 38 Sample S2 Bok Choy Bifenthrin Result vs Methodology

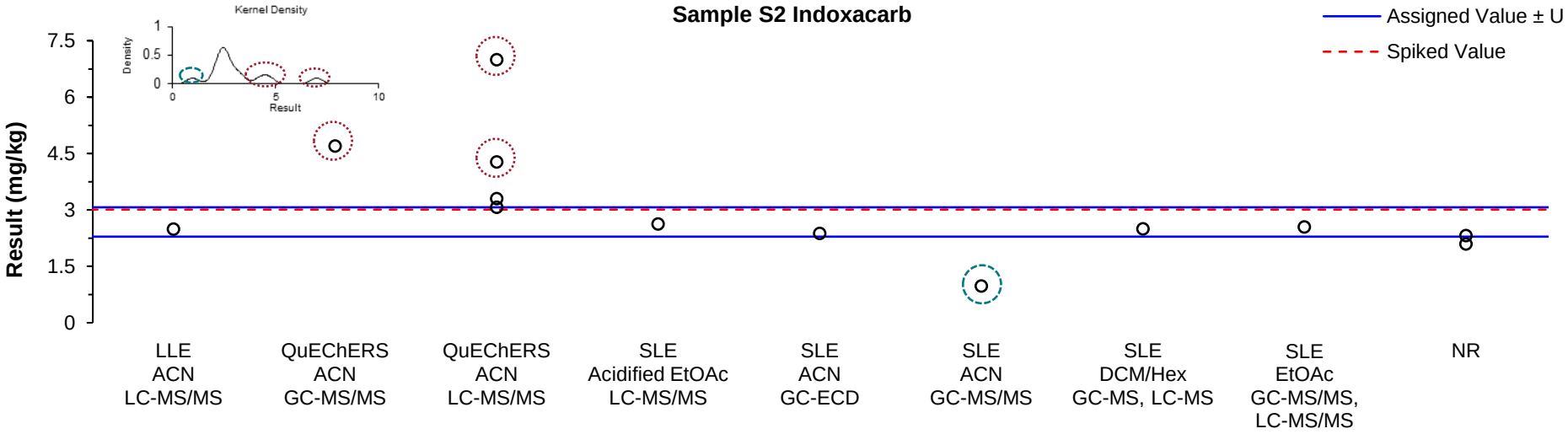


Figure 39 Sample S2 Bok Choy Indoxacarb Result vs Methodology

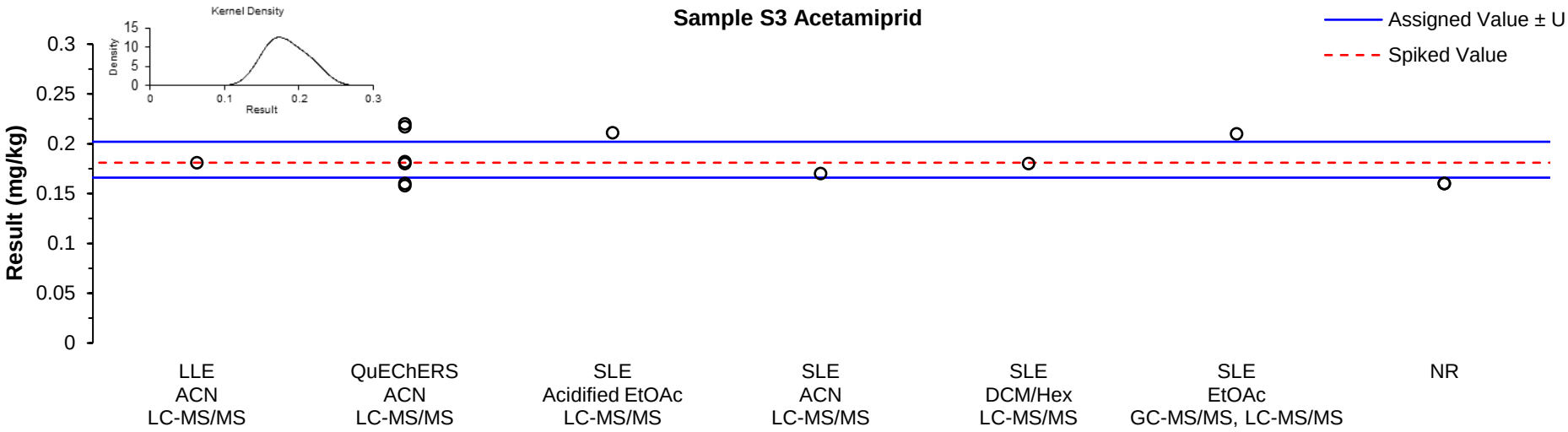


Figure 40 Sample S3 Grape Acetamiprid Result vs Methodology

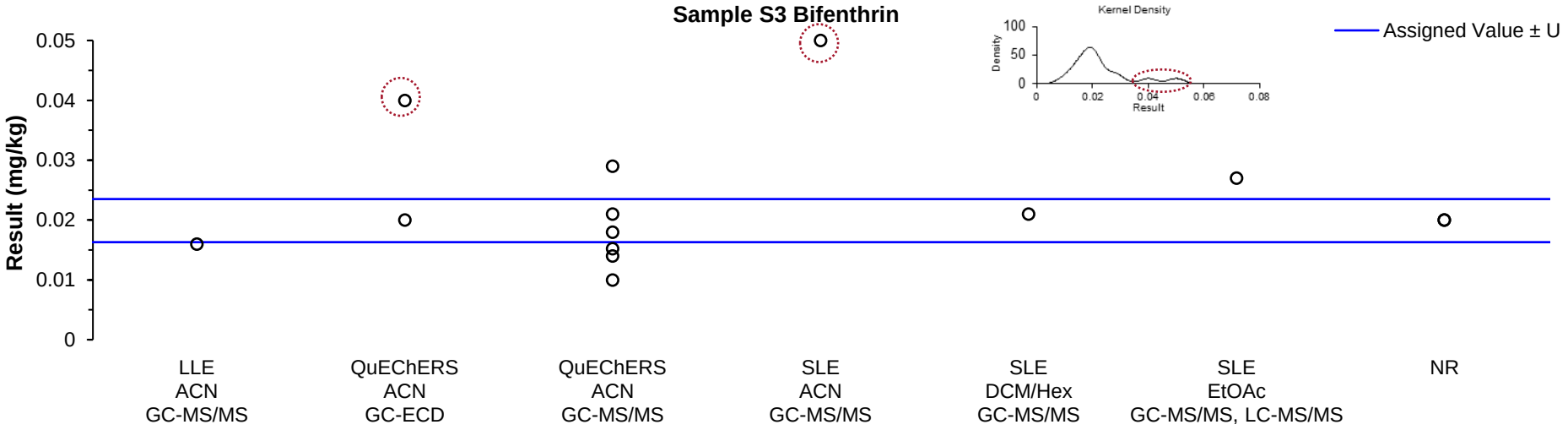


Figure 41 Sample S3 Grape Bifenthrin Result vs Methodology

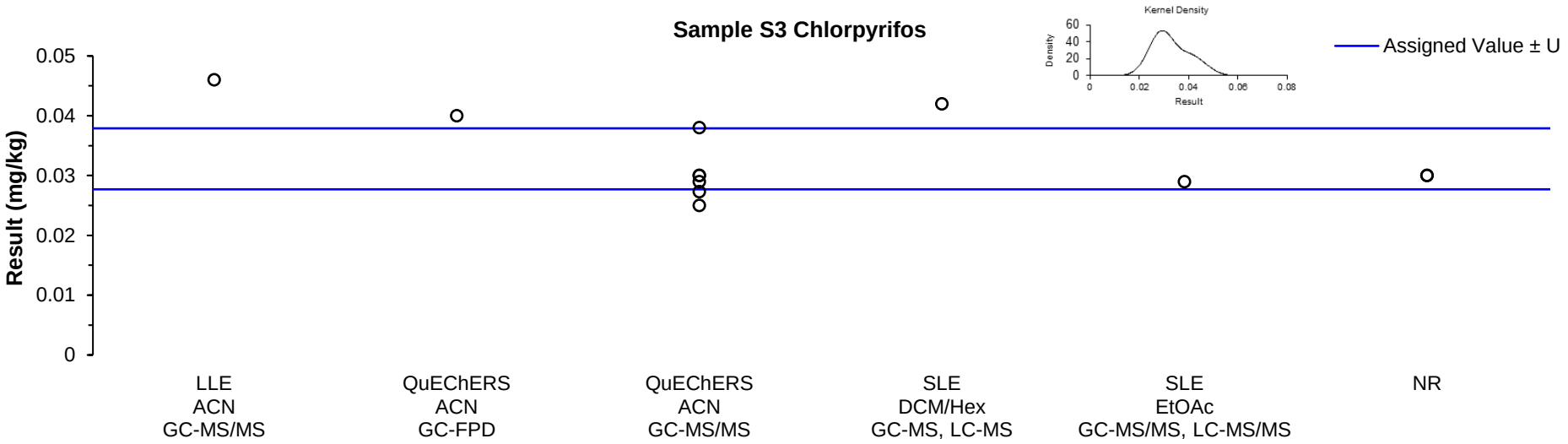


Figure 42 Sample S3 Grape Chlorpyrifos Result vs Methodology

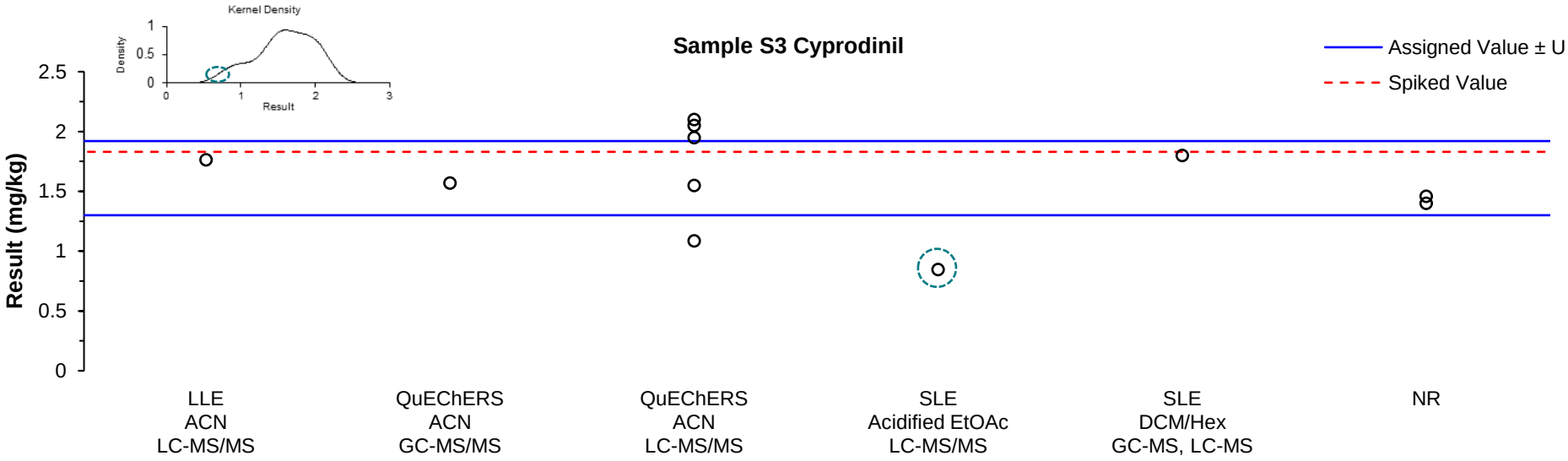


Figure 43 Sample S3 Grape Cyprodinil Result vs Methodology

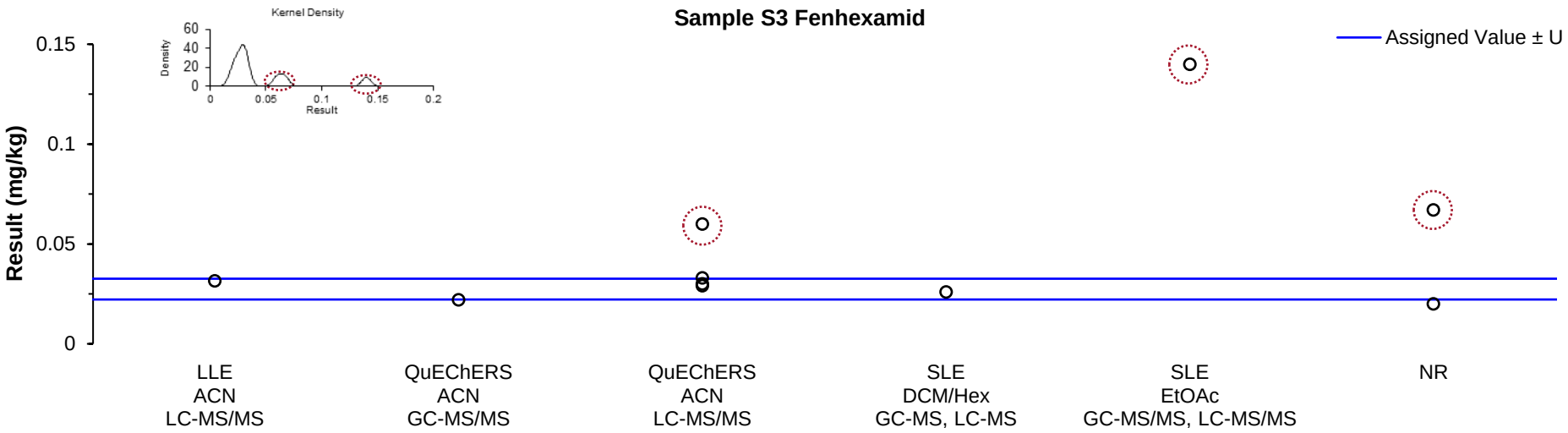


Figure 44 Sample S3 Grape Fenhexamid Result vs Methodology

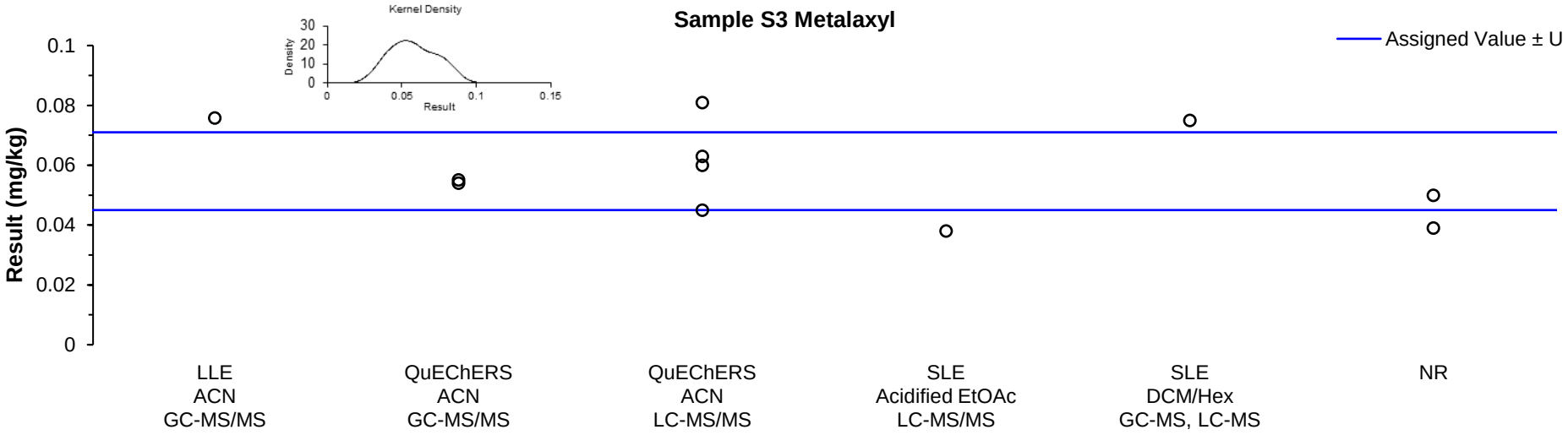


Figure 45 Sample S3 Grape Metalaxyl Result vs Methodology

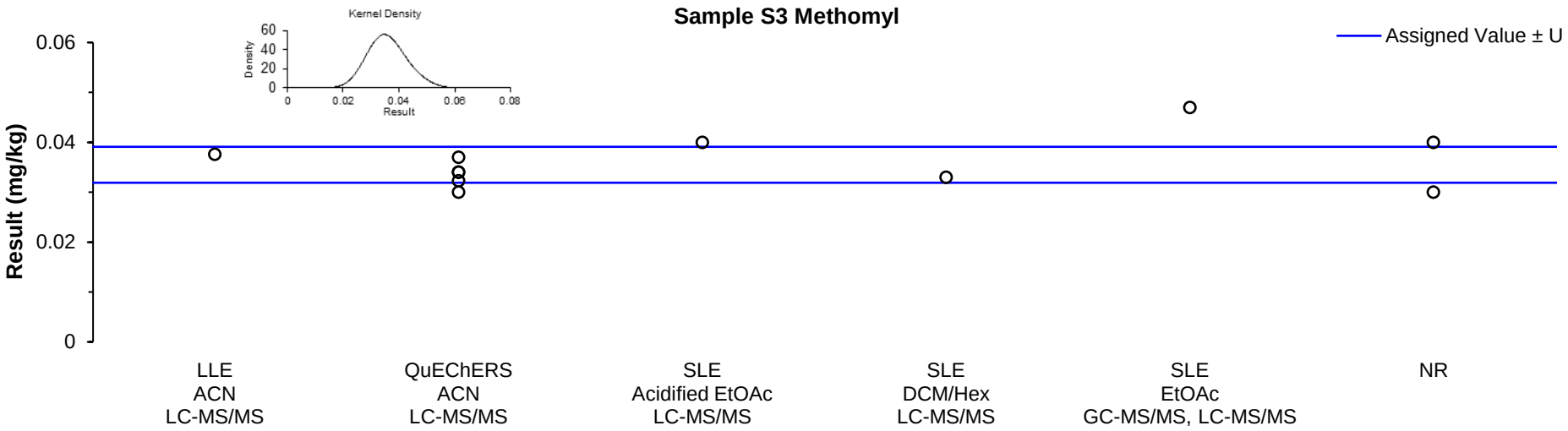


Figure 46 Sample S3 Grape Methomyl Result vs Methodology

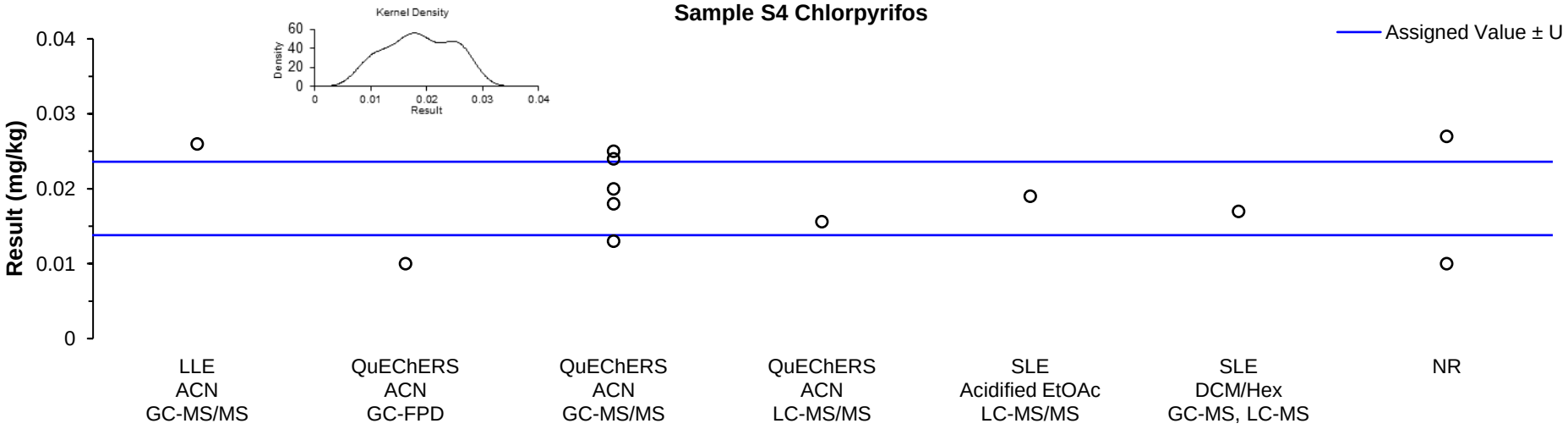


Figure 47 Sample S4 Coriander Chlorpyrifos Result vs Methodology

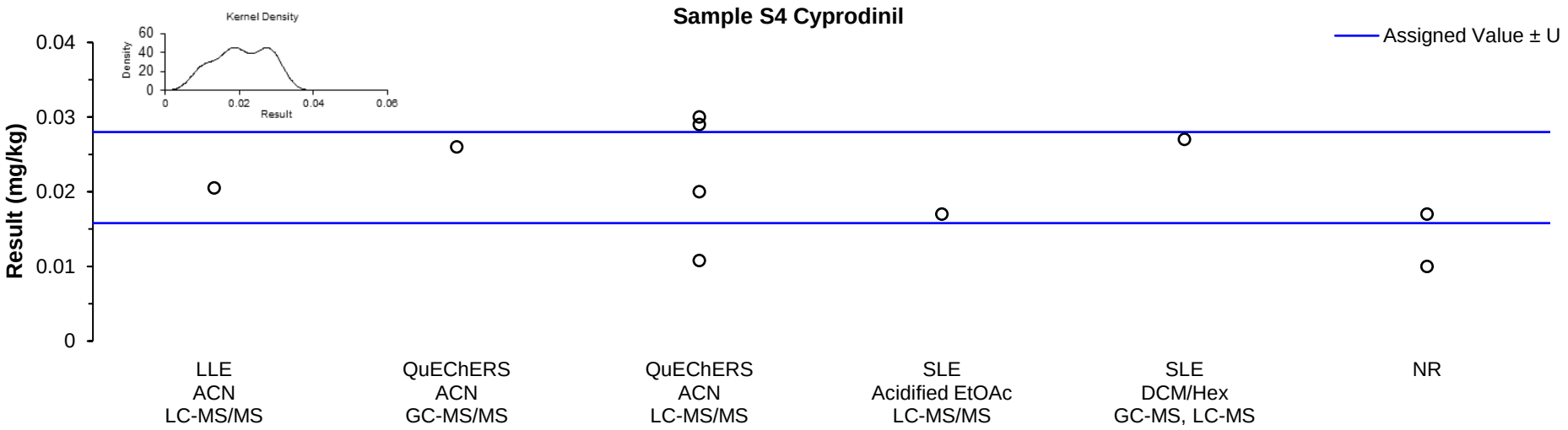


Figure 48 Sample S4 Coriander Cyprodinil Result vs Methodology

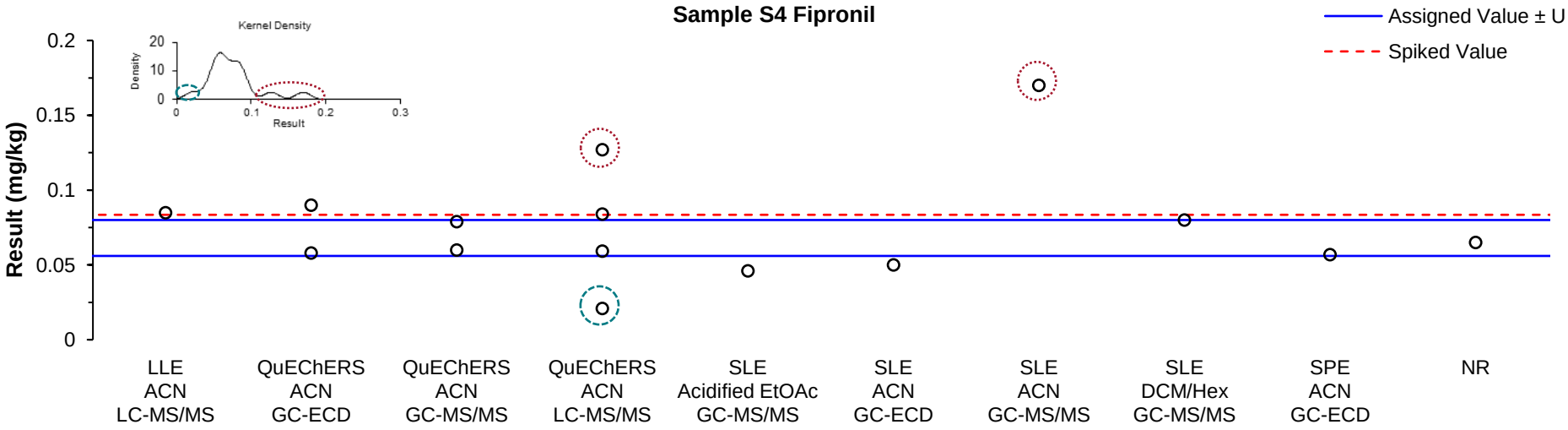


Figure 49 Sample S4 Coriander Fipronil Result vs Methodology

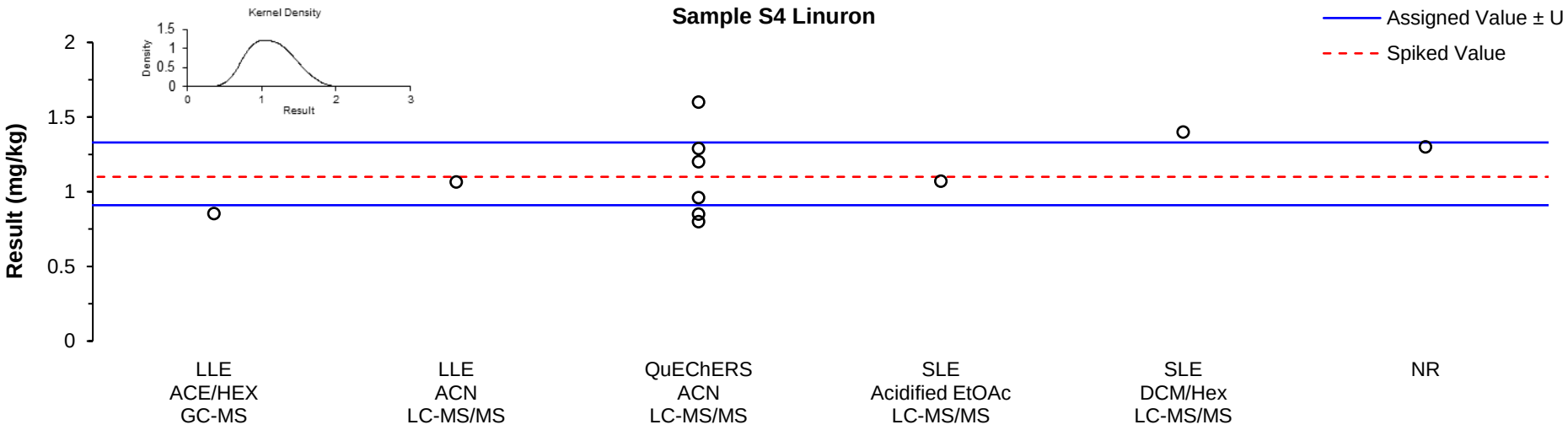


Figure 50 Sample S4 Coriander Linuron Result vs Methodology

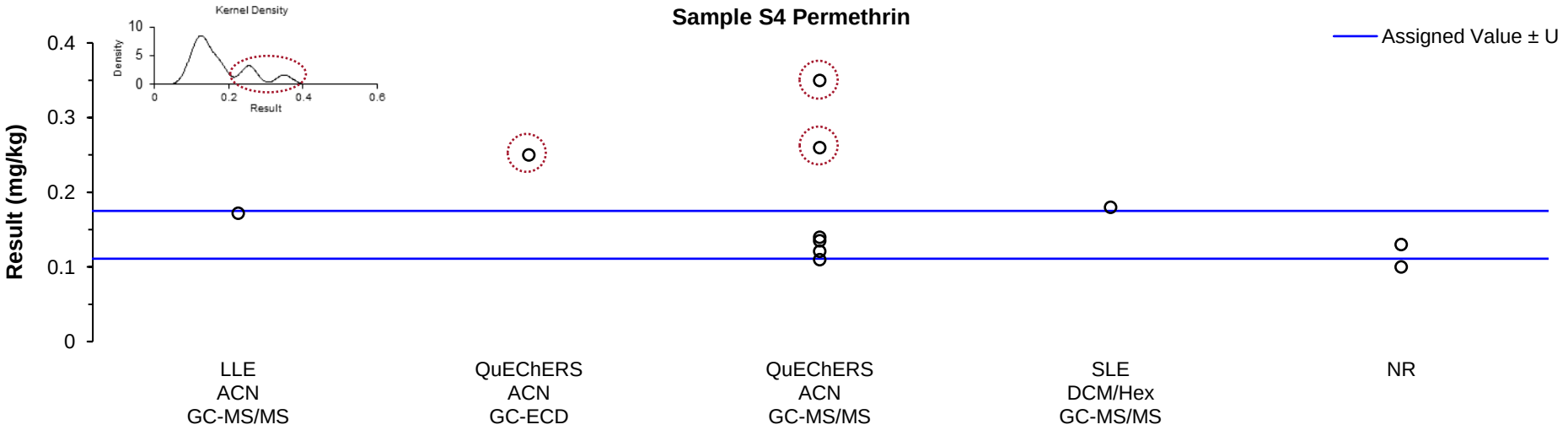


Figure 51 Sample S4 Coriander Permethrin Result vs Methodology

Participants were requested to analyse the samples using their routine test method and to report a single result as they would to a client, that is, corrected for recovery or not, according to their standard procedure. Results reported in this way reflect the true variability of results reported by laboratories to clients. Laboratories **1**, **2**, **3**, **4**, **6**, **8**, **9**, **10**, **11**, **12**, **13**, **14**, **15**, **16**, **17**, **18**, **19**, **20** and **21** reported recoveries for at least one analyte in this study, and the recoveries reported were within the range of 55% to 410%. Laboratories **2**, **3**, **7**, **8**, **11**, **13**, **16**, **17** and **19** reported that they corrected their results for recovery.

Participants were also provided with unspiked samples to be analysed if part of their routine procedures (however were instructed not to correct the spiked sample results for any analytes detected in the unspiked samples). Laboratories **1**, **2**, **3**, **4**, **5**, **7**, **8**, **10**, **11**, **12**, **13**, **14**, **15**, **16**, **17**, **18**, **20** and **21** reported analysing the unspiked samples.

6.10 Certified Reference Materials (CRM)

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

- AccuStandards
- Cambridge Isotope Laboratories
- Dr. Ehrenstorfer
- ISO 17034 certified standards
- Certified or reference compounds from other suppliers, or laboratory control samples

These materials may or may not meet the internationally recognised definition of a Certified Reference Material:

> *'**reference material**, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures'*[13]

6.11 Effect of Sample Matrix

The samples in this study were purees of tomato (Sample S1), bok choy (Sample S2), grape (Sample S3) and coriander (Sample S4). A summary of the results reported and satisfactory *z*-scores obtained for each matrix is presented in Table 32. The proportion of numeric results reported relative to expected number of results ranged from 53% to 70%, and the proportion of satisfactory *z*-scores obtained ranged from 69% to 87%. Tomato had the highest proportion of numeric results reported, while grape had the highest proportion of satisfactory *z*-scores.

Table 32 Result Comparison by Matrix

Sample	Matrix	Expected Number of Results	Numeric Results Reported	*z*-Scores	Satisfactory *z*-Scores
S1	Tomato	84	59 (70%)	47	33 (70%)
S2	Bok Choy	63	43 (68%)	29	20 (69%)
S3	Grape	168	91 (54%)	82	71 (87%)
S4	Coriander	147	78 (53%)	59	47 (80%)

6.12 Summary of Participants' Results and Performances

Summaries of participants' results and performances for scored analytes in this PT study are presented in Tables 33 and 34, and Figure 52.

Table 33 Summary of Participants' Samples S1 and S2 Results*

Lab. Code	Sample S1			Sample S2	
	Chlorpyrifos	Endosulfan sulfate	Fenhexamid	Bifenthrin	Indoxacarb
AV	0.732	0.426	0.464	0.0158	2.68
SV	0.821	0.447	0.502	0.0167	3.01
1	0.86	0.49	0.43	0.014	2.5
2	0.85	0.39	NT	0.02	NT
3	0.62	0.25	0.85	NR	NT
4	0.71	0.42	0.467	0.018	3.3
5	0.59	0.31	0.49	0.028	7
6	0.82	0.43	0.29	0.026	4.70
7	1.086	0.666	0.4701	0.014	2.4896
8	0.723	0.537	NT	NT	NT
9	0.66	0.501	0.702	0.016	4.28
10	0.77	0.64	NT	NR	NT
11	0.255	0.156	0.370	0.012	2.630
12	0.84	NT	0.46	0.01	2.32
13	NT	NT	NT	NT	NT
14	0.663	0.428	NT	0.136	NT
15	NT	NT	NT	0.02	2.55
16	0.32	0.64	NT	0.02	0.98
17	0.72	0.42	0.56	0.016	2.1
18	0.28	0.36	NT	<0.01	2.38
19	0.237	0.348	NT	0.0202	NT
20	0.868	0.428	NT	0.0142	3.077
21	0.20	0.31	NT	0.011	NT

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

Table 34 Summary of Participants' Samples S3 and S4 Results*

Lab. Code	Sample S3							Sample S4				
	Acetamiprid	Bifenthrin	Chlorpyrifos	Cyprodinil	Fenhexamid	Metalaxyl	Methomyl	Chlorpyrifos	Cyprodinil	Fipronil	Linuron	Permethrin
AV	0.184	0.0199	0.0328	1.61	0.0274	0.058	0.0355	0.0187	0.0219	0.068	1.12	0.143
SV	0.181	-	-	1.83	-	-	-	-	-	0.0835	1.10	-
1	0.18	0.021	0.042	1.8	0.026	0.075	0.033	0.017	0.027	0.080	1.4	0.18
2	NT	0.04	NR	NT	NT	NT	NT	NR	NT	0.09	NT	0.25
3	0.22	0.01	0.03	1.95	0.06	0.06	0.03	0.02	0.03	0.06	0.8	0.11
4	0.158	0.018	0.025	1.55	0.029	0.063	0.034	0.025	0.029	0.127	1.6	0.35
5	0.18	0.014	0.029	2.1	0.03	0.081	NR	0.024	NR	0.021	1.2	0.14
6	0.16	0.029	0.038	1.569	0.022	0.054	0.034	0.018	0.026	0.079	0.85	0.26
7	0.1808	0.016	0.046	1.7644	0.0315	0.0758	0.0376	0.026	0.0205	0.085	1.0661	0.172
8	NT	NT	NT	NT	NT	NT	NT	NT	NT	0.058	NT	NT
9	0.217	0.021	0.03	2.05	0.033	0.045	0.037	0.013	0.02	0.084	1.29	0.121
10	NT	0.02	0.04	NT	NT	NT	NT	0.01	NT	NT	NT	NR
11	0.211	<0.02	<0.02	0.847	<0.02	0.038	0.040	0.019	0.017	0.046	1.071	NT
12	0.16	0.02	0.03	1.46	0.02	0.05	0.03	0.01	0.01	NT	NT	NT
13	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	0.854	NT
14	NT	NR	NR	NT	NT	NT	NT	NR	NT	NT	NT	NT
15	0.21	0.027	0.029	NT	0.14	NT	0.047	NT	NT	NT	NT	NT
16	0.17	0.05	NR	NT	NT	NT	NT	NR	NT	0.17	NT	0.13
17	0.16	0.020	0.03	1.4	0.067	0.039	0.040	0.027	0.017	0.065	1.3	0.10
18	NT	<0.01	<0.01	NT	NT	NT	NT	<0.01	NT	0.05	NT	<0.01
19	NT	NR	NR	NT	NT	NR	NT	NR	NT	NR	NT	NR
20	0.182	0.0152	0.0273	1.087	NT	0.0551	0.0323	0.0156	0.0108	0.0592	0.960	0.135
21	NT	<0.01	<0.01	NT	NT	NT	NT	<0.01	NT	0.057	NT	<0.01

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

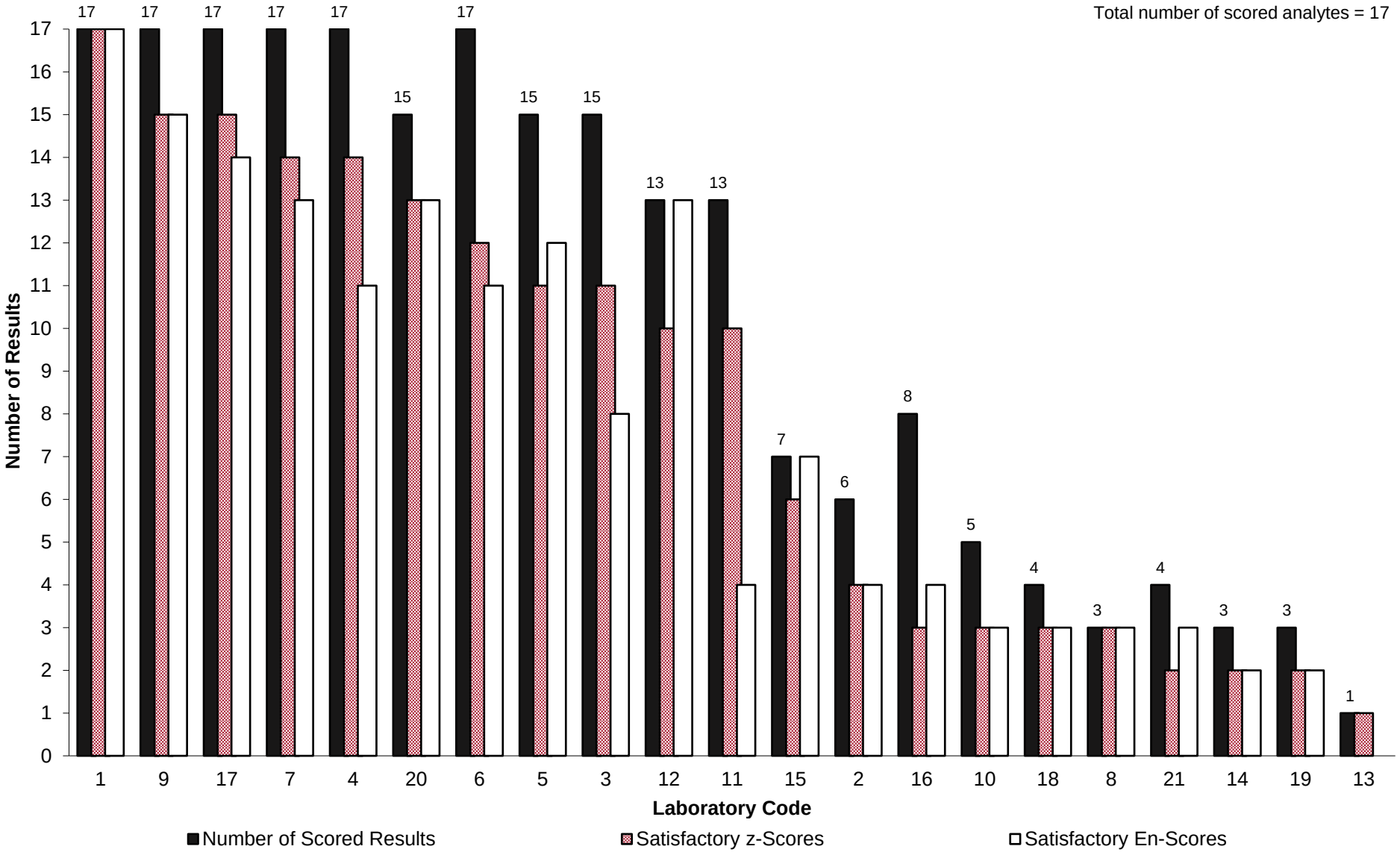


Figure 52 Summary of Participants' Performance

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

A summary of participation and reported results rates in NMI Pesticides in Fruit, Vegetables and Herbs PT studies over the last 10 studies (2015 to 2023) is presented in Figure 53. While the number of spiked analytes per study has increased, the numeric results reported by participants have remained fairly steady.

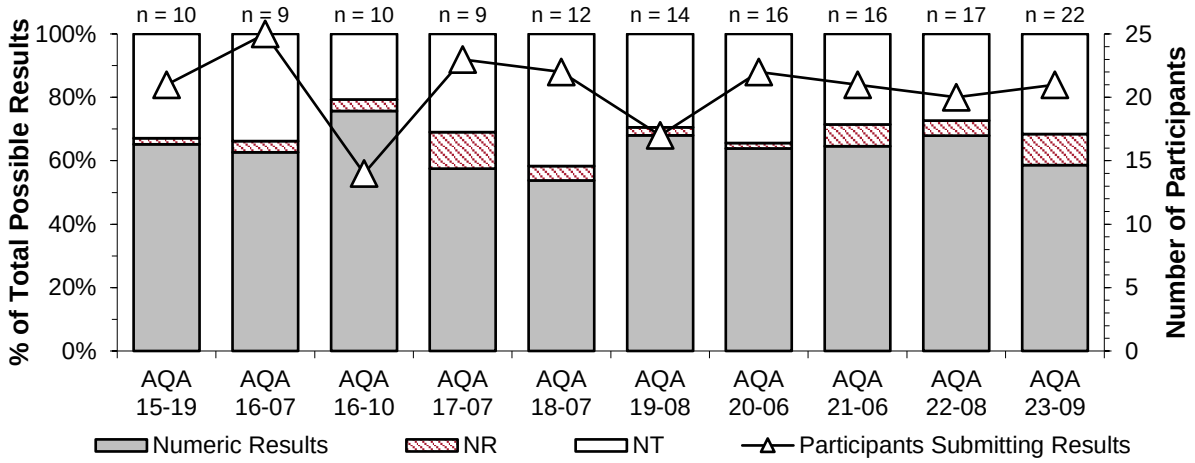


Figure 53 Summary of Participation and Reported Results in NMI Pesticides in Fruit, Vegetables and Herbs PT Studies (n = number of assessed analytes)

A summary of the satisfactory performance (presented as a percentage of the total number of scores for each study) in NMI Pesticides in Fruit, Vegetables and Herbs PT studies over the last 10 studies (2015 to 2023) is presented in Figure 54. The target SD used to calculate *z*-scores has been kept constant at 15% PCV, except for the incurred analytes and the herb matrix in this study where 20% PCV was used. Over this period, the average proportion of satisfactory scores was 77% for *z*-scores and 70% for E_n-scores.

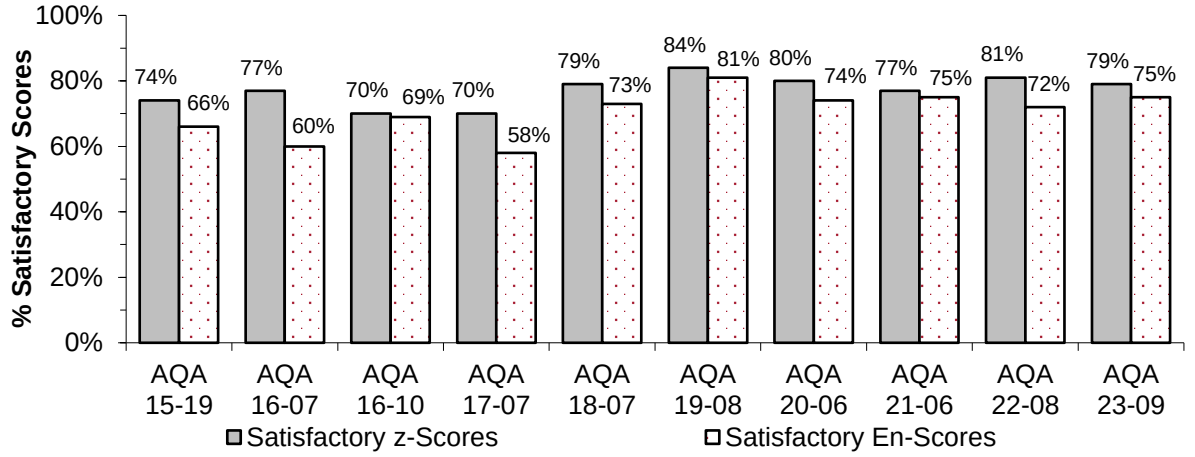


Figure 54 Summary of Participants' Performance in NMI Pesticides in Fruit, Vegetables and Herbs PT Studies

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

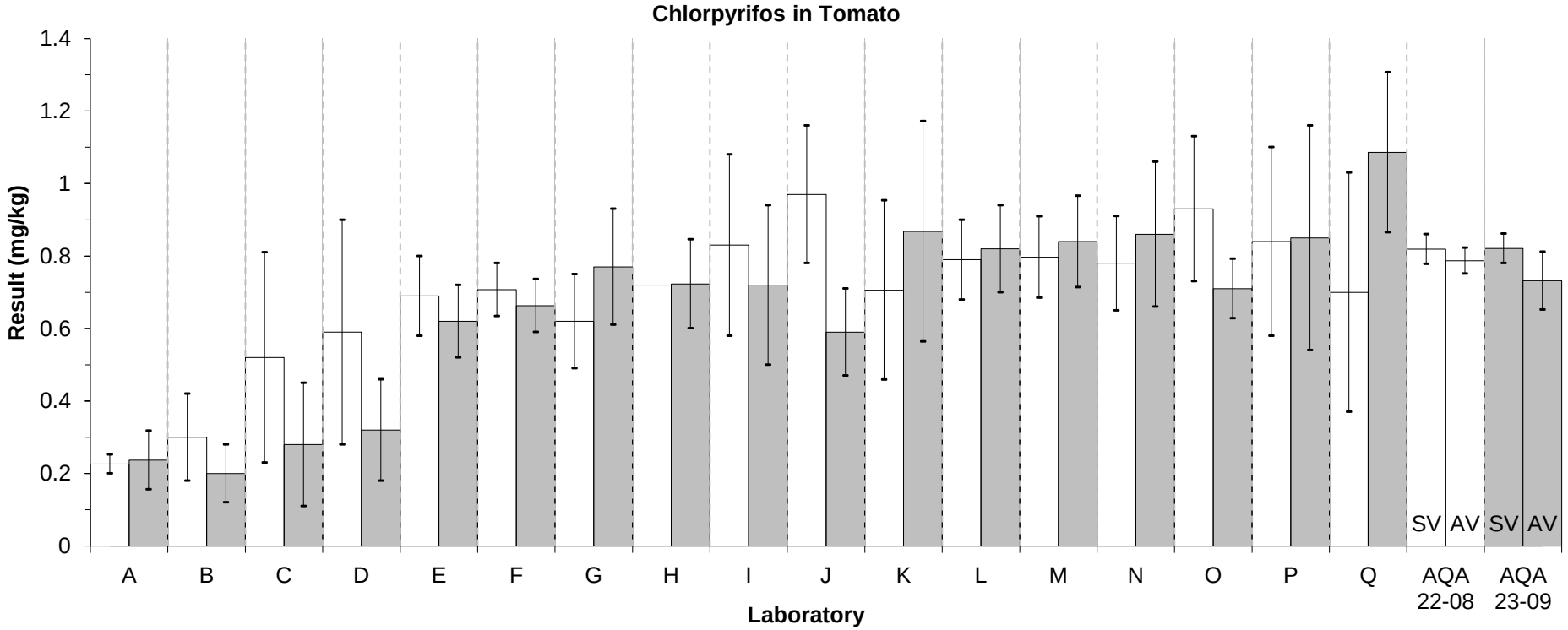
Chlorpyrifos in Tomato

For this study, chlorpyrifos was spiked into Sample S1 (tomato) at the same level as for last year's PT study AQA 22-08 Sample S1 (also tomato).

Participants' results for chlorpyrifos in tomato over these two studies are shown in Figure 55, for participants who reported results in both studies. Most participants reported similar results for both studies, and for all except one participant (Laboratory J in Figure 55), results were in agreement with each other within their reported expanded uncertainties.

Variability of participants' results was greater in AQA 23-09 than in AQA 22-08.

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



SV = Spiked Value; AV = Assigned Value. Shaded columns correspond to results from this study, AQA 23-09.

Figure 55 AQA 22-08 and AQA 23-09 Chlorpyrifos in Tomato Results

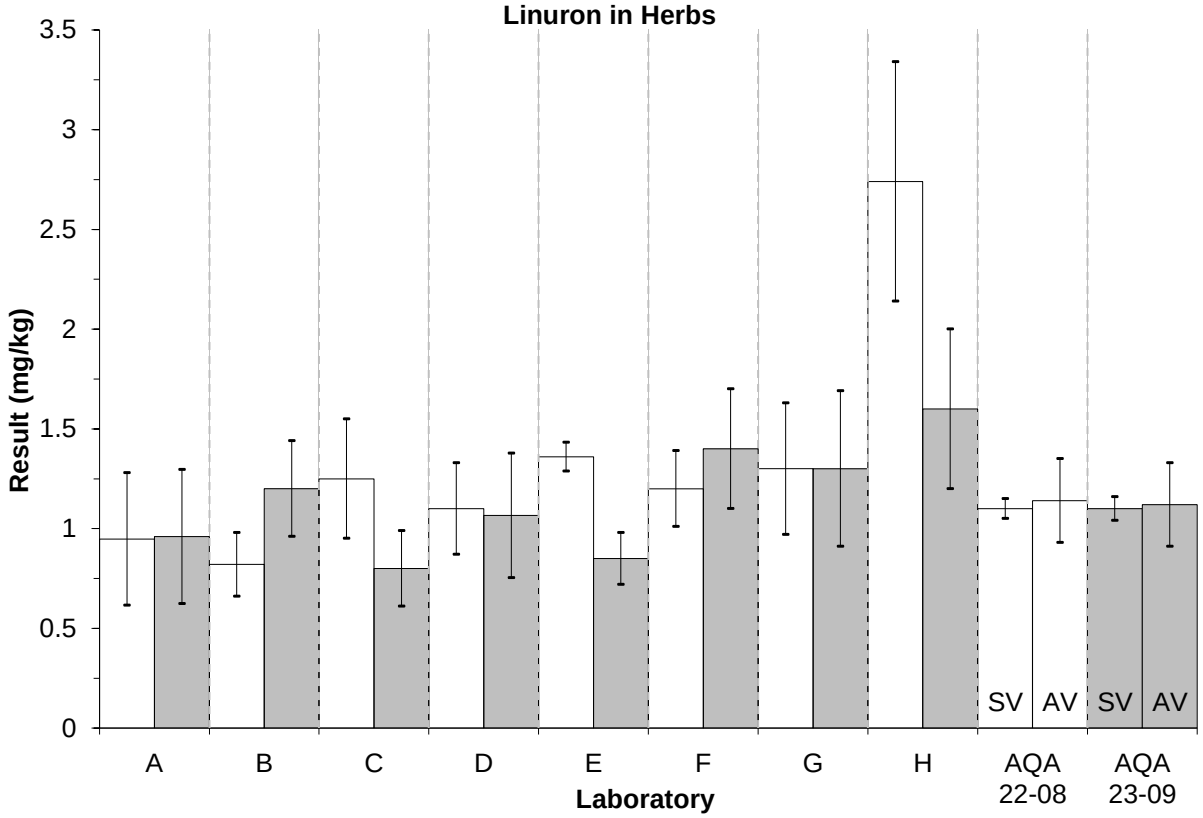
Linuron in Herbs

For this study, Sample S4 (coriander) was spiked with linuron at the same level as last year's PT study AQA 22-08 Sample S3 (parsley).

Results for linuron in herbs over these two studies are shown in Figure 56, grouped by participant where the participant reported results in both studies. Most participants reported similar results for both studies, and for all except two participants (Laboratory E and H in Figure 56), results agreed with each other within their reported expanded uncertainties.

There was similar variability of participants' results for both studies.

In both studies, the assigned values and the spiked values agreed with each other within their respective expanded uncertainties.



SV = Spiked Value; AV = Assigned Value. Shaded columns correspond to results from this study, AQA 23-09.

Figure 56 AQA 22-08 and AQA 23-09 Linuron in Herbs Result

7 REFERENCES

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

[1] ISO/IEC 17043:2010, *Conformity assessment – General requirements for proficiency testing.*

[2] NMI, 2023, *Study Protocol for Proficiency Testing*, viewed August 2023, <https://www.industry.gov.au/sites/default/files/2020-10/cpt_study_protocol.pdf>.

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[12] 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.

[13] BIPM, JCGM 200:2012, *International vocabulary of metrology – Basic and general concepts and associated terms (VIM)*, 3rd edition, viewed August 2023, <https://www.bipm.org/utils/common/documents/jcgm/JCGM_200_2012.pdf>.

[14] Federal Register of Legislation, 2022, *Australia New Zealand Food Standards Code – Schedule 22 – Foods and classes of foods*, viewed August 2023, <https://www.legislation.gov.au/Details/F2022C00970>.

APPENDIX 1 SAMPLE PREPARATION

Tomatoes and bok choy were bought from a local organic fruit and vegetable wholesaler. Grapes and coriander were bought from local grocery stores. The portion of the fruit, vegetables and herbs prepared was in accordance with the Australian New Zealand Food Standards Code – Schedule 22 – Foods and classes of foods.[14]

Preparation of Sample S1 (Tomato)

The tomatoes were rinsed using tap water and allowed to air dry. The tomatoes (including the peel) were chopped and placed in a stainless steel drum, pureed with a stick mixer and passed through an 850 µm sieve. The sieved puree was continuously stirred while 35 aliquots of at least 100 g were dispensed into 200 mL amber bottles to provide unspiked samples. The remaining puree was spiked with aliquots of each pesticide standard solution. The spiked puree was stirred for at least two hours and bottled. Each bottle was then labelled, shrink-wrapped and placed in a freezer.

Preparation of Sample S2 (Bok Choy)

The bok choy was rinsed using tap water and allowed to air dry. The bok choy was then chopped, placed in a stainless steel drum, pureed with a stick mixer and passed through an 850 µm sieve. The sieved puree was continuously stirred while 35 aliquots of at least 100 g were dispensed into 200 mL amber bottles to provide unspiked samples. The remaining puree was spiked with aliquots of each pesticide standard solution. The spiked puree was stirred for at least two hours and bottled. Each bottle was then labelled, shrink-wrapped and placed in a freezer.

Preparation of Sample S3 (Grape)

The grapes were rinsed with tap water and allowed to air dry. The grapes were then placed into a stainless steel drum, pureed with a stick mixer, and passed through an 850 µm sieve. The puree was continuously stirred while 35 aliquots of at least 100 g were dispensed into 200 mL amber bottles to provide unspiked samples. The remaining puree was spiked with aliquots of each pesticide standard solution. The spiked puree was stirred for at least two hours and bottled. Each bottle was then labelled, shrink-wrapped and placed in a freezer.

Preparation of Sample S4 (Coriander)

The coriander was rinsed with tap water. The coriander was placed in a stainless steel drum, pureed with a stick mixer, and passed through an 850 µm sieve. The puree was continuously stirred while 35 aliquots of at least 50 g were dispensed into 100 mL amber bottles to provide unspiked samples. The remaining puree was spiked with aliquots of each pesticide standard solution. The spiked puree was stirred for at least two hours and bottled. Each bottle was then labelled, shrink-wrapped and placed in a freezer.

APPENDIX 2 HOMOGENEITY AND STABILITY

A2.1 Homogeneity

No homogeneity testing was completed for this study as the samples were prepared using a process demonstrated in previous NMI PT studies to produce sufficiently homogeneous samples. The results of this study also gave no reason to question the samples' homogeneity. Comparisons of results for all scored analytes to bottle number analysed by participants are presented in Figures 57 to 73. Results have only been included if the bottle number was known (i.e. when the participant was sent only one sample set), and extreme outliers have been removed. No fill order trend was observed.

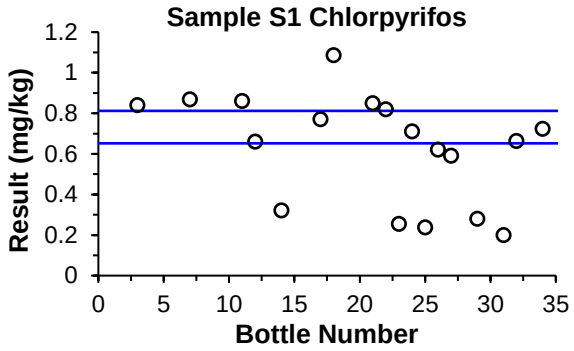

Figure 57 S1 Chlorpyrifos Result vs Bottle Number

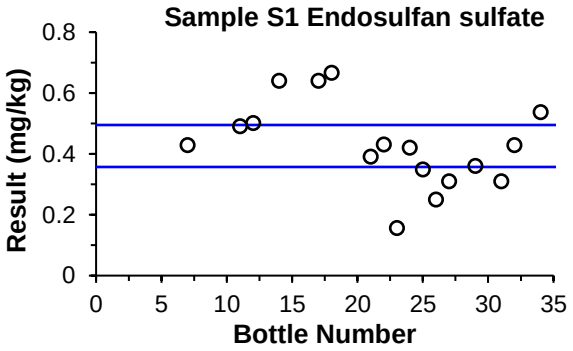

Figure 58 S1 Endosulfan Sulfate Result vs Bottle Number

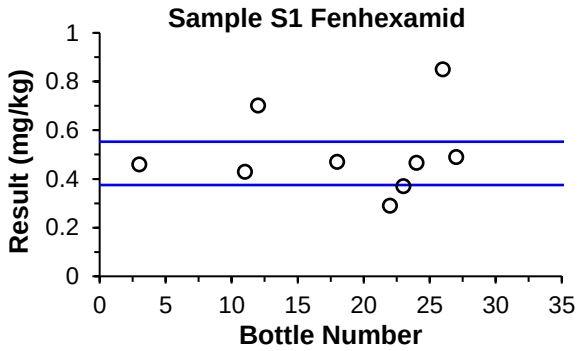

Figure 59 S1 Fenhexamid Result vs Bottle Number

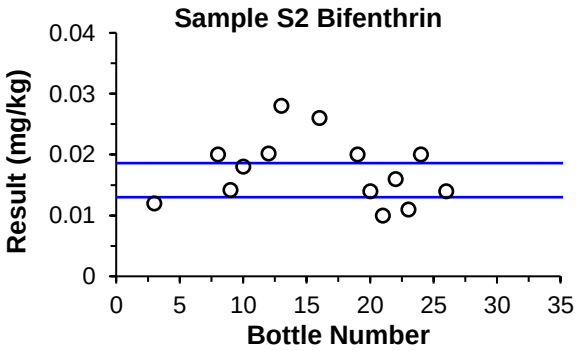

Figure 60 S2 Bifenthrin Result vs Bottle Number

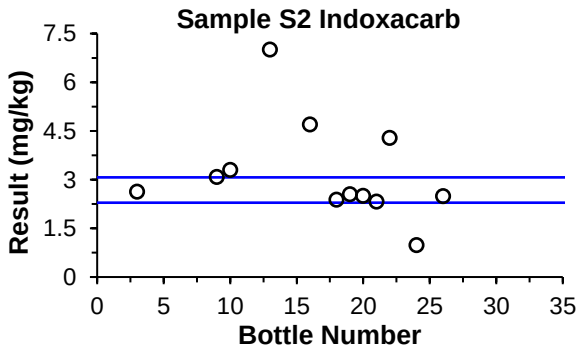

Figure 61 S2 Indoxacarb Result vs Bottle Number

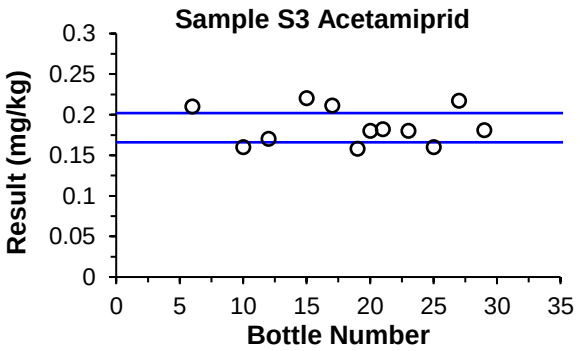

Figure 62 S3 Acetamiprid Result vs Bottle Number

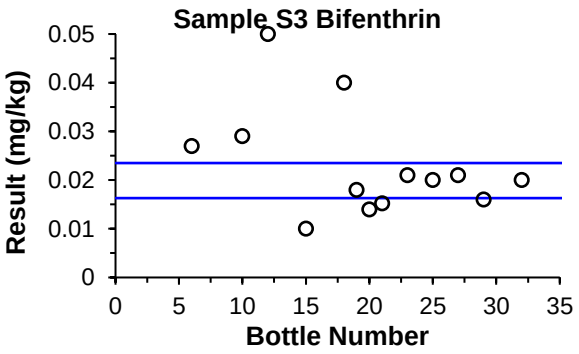

Figure 63 S3 Bifenthrin Result vs Bottle Number

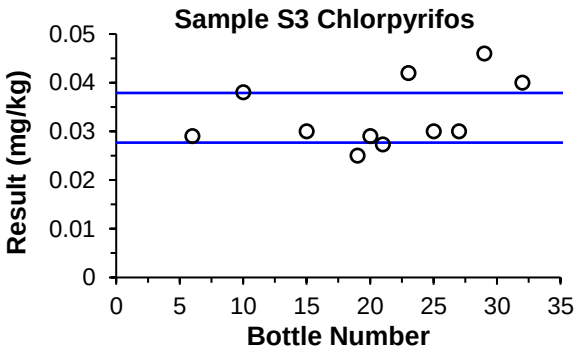

Figure 64 S3 Chlorpyrifos Result vs Bottle Number

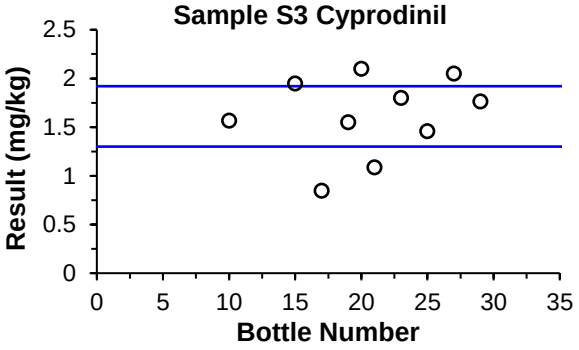

Figure 65 S3 Cyprodinil Result vs Bottle Number

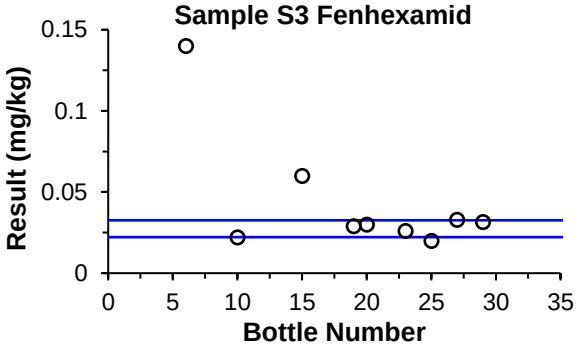

Figure 66 S3 Fenhexamid Result vs Bottle Number

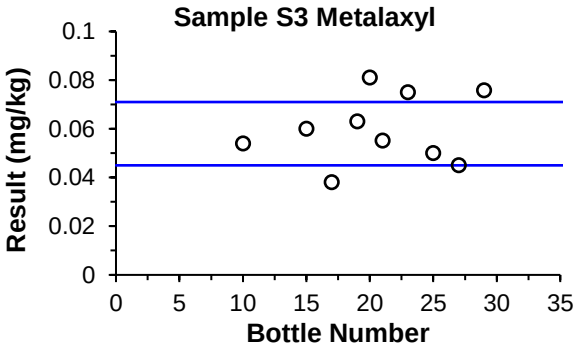

Figure 67 S3 Metalaxyl Result vs Bottle Number

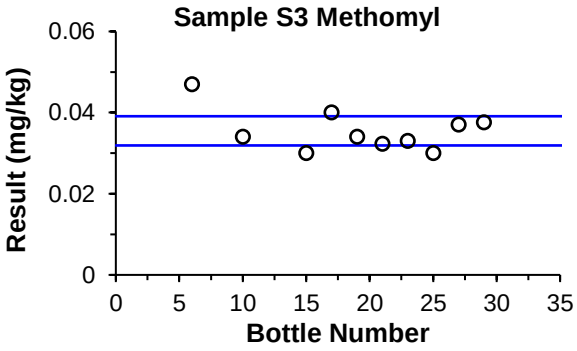

Figure 68 S3 Methomyl Result vs Bottle Number

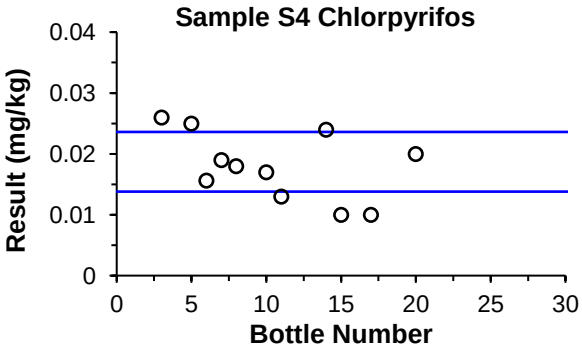

Figure 69 S4 Chlorpyrifos Result vs Bottle Number

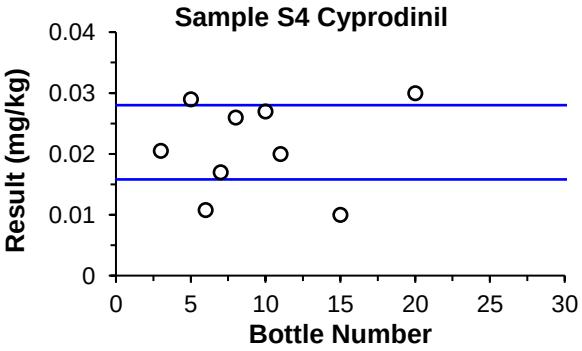

Figure 70 S4 Cyprodinil Result vs Bottle Number

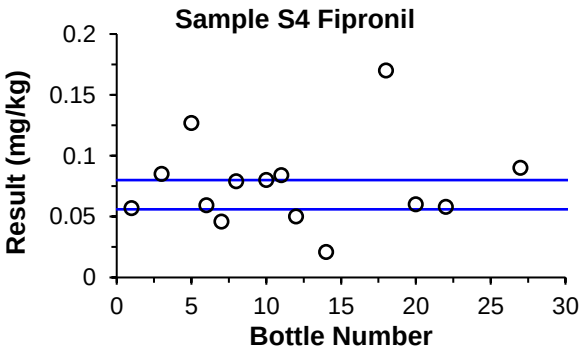

Figure 71 S4 Fipronil Result vs Bottle Number

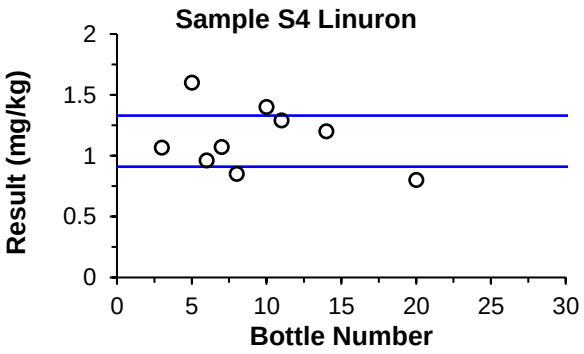

Figure 72 S4 Linuron Result vs Bottle Number

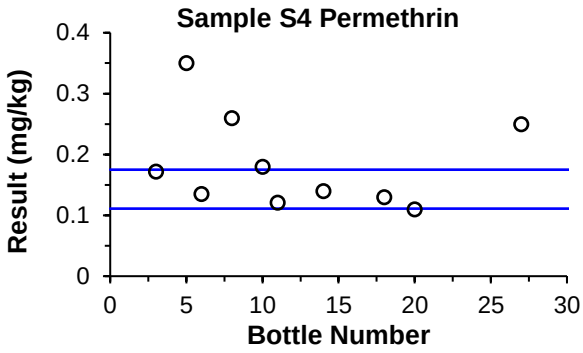

Figure 73 S4 Permethrin Result vs Bottle Number

A2.2 Stability

No stability testing was conducted for this study as the process used to prepare, store and dispatch the samples was demonstrated in previous NMI PT studies to produce sufficiently stable samples. The samples were stored in a freezer at approximately -20 °C after preparation and prior to dispatch. The samples were dispatched to participants in insulated polystyrene foam boxes with cooler bricks.

Participants' results in this study gave no reason to question the samples' transportation stability. Comparisons of results for all scored analytes to days spent in transit, are presented in Figures 74 to 90; no evidence of analyte degradation in transit was observed.

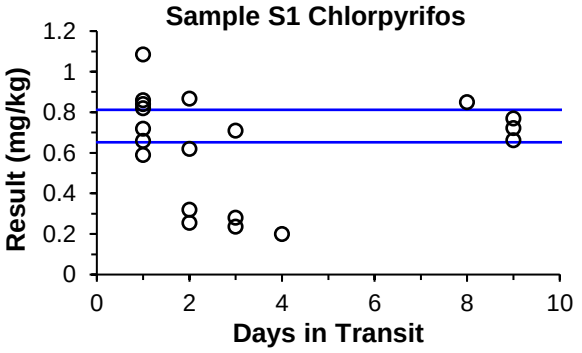

Figure 74 S1 Chlorpyrifos Result vs Transit Days

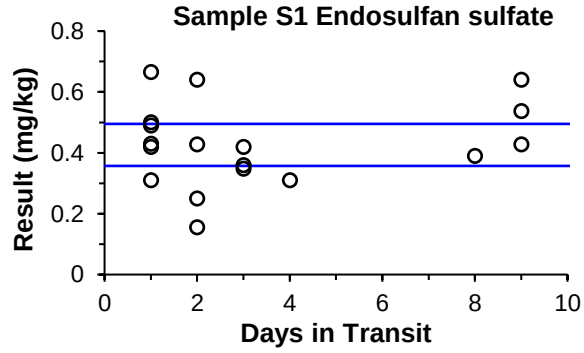

Figure 75 S1 Endosulfan Sulfate Result vs Transit Days

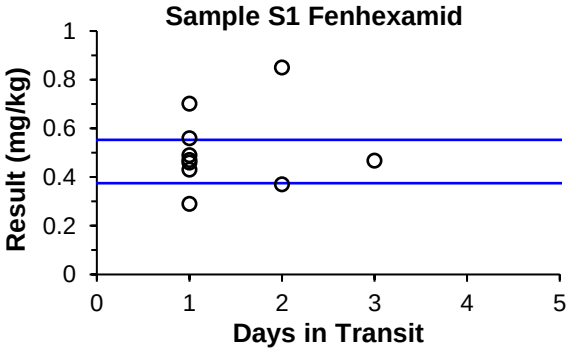

Figure 76 S1 Fenhexamid Result vs Transit Days

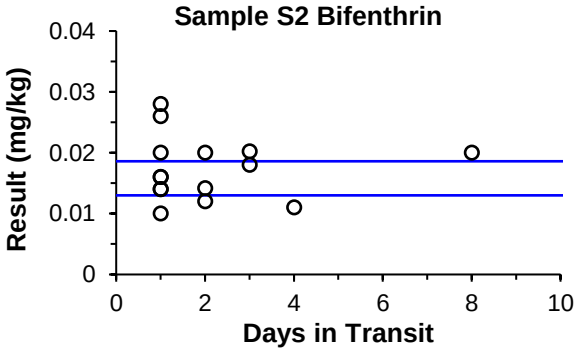

Figure 77 S2 Bifenthrin Result vs Transit Days

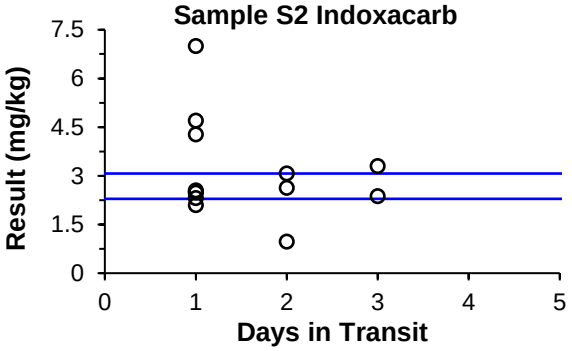

Figure 78 S2 Indoxacarb Result vs Transit Days

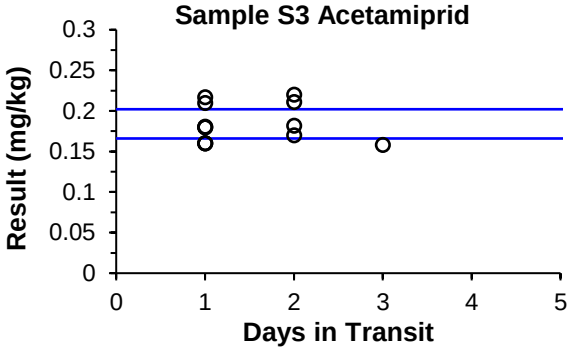

Figure 79 S3 Acetamiprid Result vs Transit Days

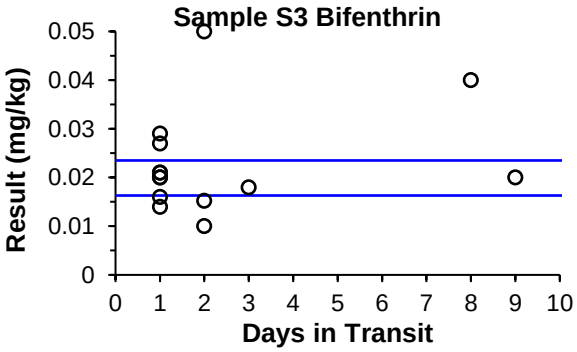

Figure 80 S3 Bifenthrin Result vs Transit Days

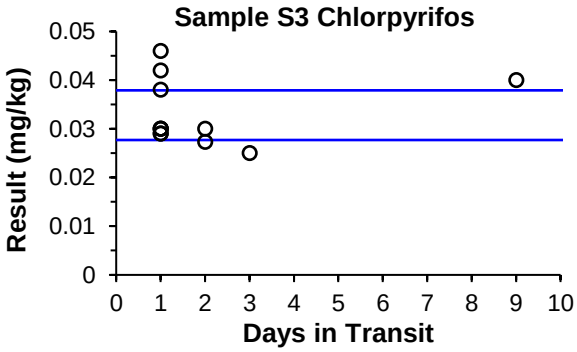

Figure 81 S3 Chlorpyrifos Result vs Transit Days

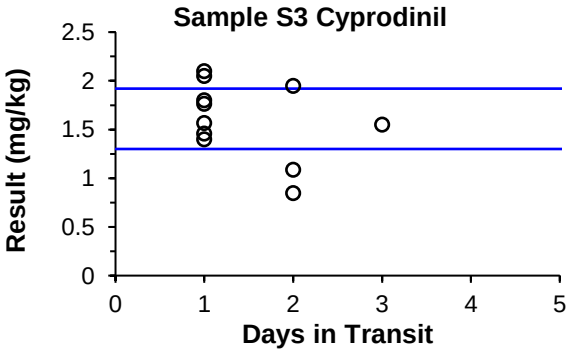

Figure 82 S3 Cyprodinil Result vs Transit Days

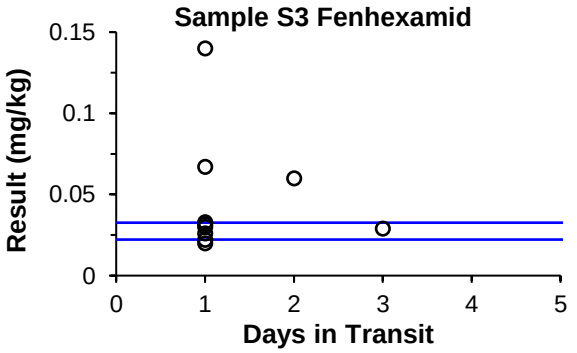

Figure 83 S3 Fenhexamid Result vs Transit Days

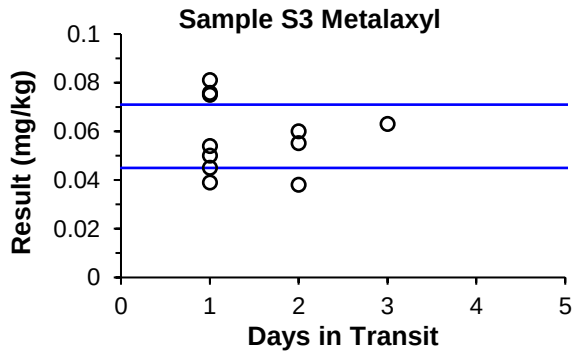

Figure 84 S3 Metalaxyl Result vs Transit Days

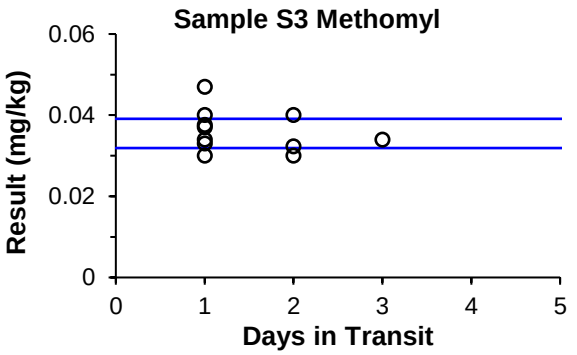

Figure 85 S3 Methomyl Result vs Transit Days

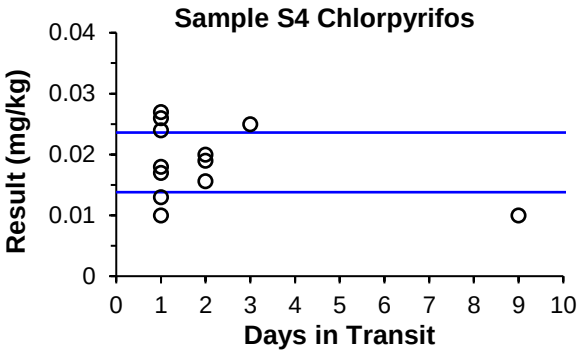

Figure 86 S4 Chlorpyrifos Result vs Transit Days

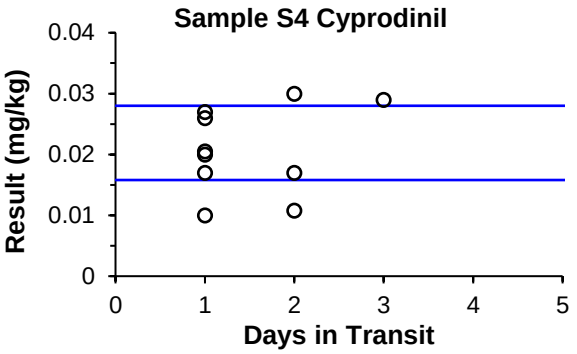

Figure 87 S4 Cyprodinil Result vs Transit Days

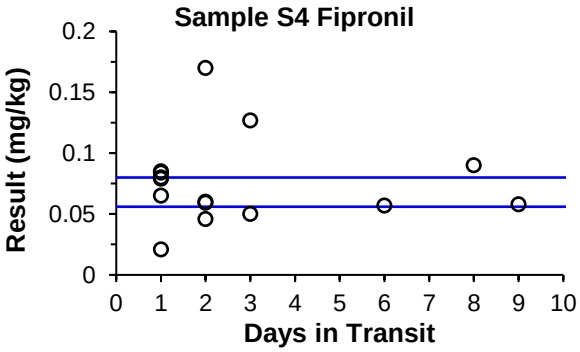

Figure 88 S4 Fipronil Result vs Transit Days

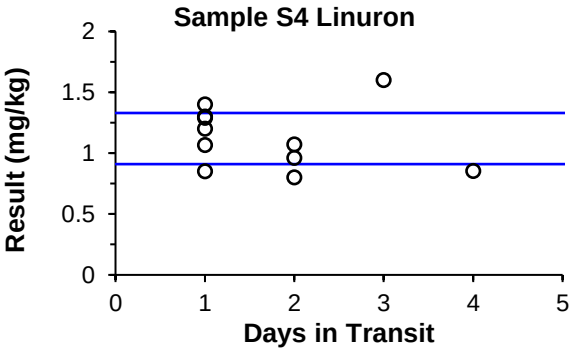

Figure 89 S4 Linuron Result vs Transit Days

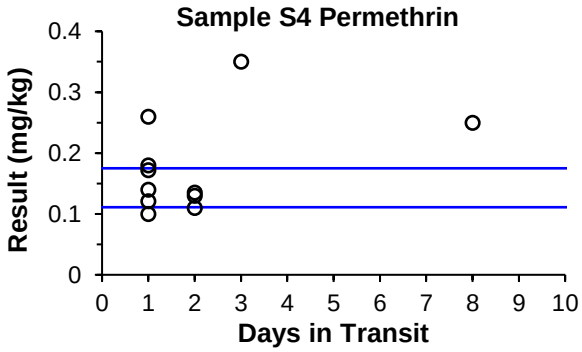

Figure 90 S4 Permethrin Result vs Transit Days

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

A3.1 Robust Average and Associated Uncertainty

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

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

where:

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

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

p is the number of results

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

A worked example for Sample S3 acetamiprid is set out below in Table 35.

Table 35 Uncertainty of Robust Average for Sample S3 Acetamiprid

Number of results (p)	13
Robust Average	0.184 mg/kg
$S_{rob\ av}$	0.026 mg/kg
$u_{rob\ av}$	0.009 mg/kg
k	2
$U_{rob\ av}$	0.018 mg/kg

Therefore, the robust average for Sample S3 acetamiprid is 0.184 ± 0.018 mg/kg.

A3.2 *z*-Score and E_n-Score Calculation

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

A worked example for the result reported by Laboratory 1 for Sample S1 chlorpyrifos is set out below in Table 36.

Table 36 *z*-Score and E_n-Score for Sample S1 Chlorpyrifos Result Reported by Laboratory 1

Participant Result (mg/kg)	Assigned Value (mg/kg)	Target Standard Deviation	*z*-Score	E_n-Score
0.86 ± 0.2	0.732 ± 0.080	15% as CV, or: 0.15 × 0.732 = 0.1098 mg/kg	$z = \frac{0.86 - 0.732}{0.1098} = 1.17$	$E_n = \frac{0.86 - 0.732}{\sqrt{0.2^2 + 0.080^2}} = 0.59$

APPENDIX 4 PARTICIPANTS' TEST METHODS

Participants were requested to provide information about their test methods. Responses are presented in Tables 37 to 58. Some responses may be modified so that the participant cannot be identified.

Table 37 Sample S1 Tomato Chlorothalonil Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	20	Solid-Liquid	DCM,Hex		GC-MS/MS
2	NT				
3	10	QuEChERS	ACN	d-SPE	GC-MS/MS
4	10	QuEChERS	Acetonitrile	PSA	GC-MS/MS
5	10	QuEChERS	Acetonitrile	Florisil	GC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	GC-MS/MS
7	15	Liquid-Liquid	Acetonitrile	dSPE	GC-MS/MS
8	NT				
9	5	QuEChERS	0.1% Acetic acid in Acetonitrile	Dispersive SPE:- C18, MgSO4.	GC-ECD
10	20	QuEChERS	Acetonitrile	DSPE	GC-ECD
11	NT				
12	15	QuEChERS	ACN	PSA	GC-MS/MS
13	1	Liquid-Liquid	Acetone:Hexane (2:1)	GPC / Florisil	GC-MS
14	20	QuEChERS	Acetonitrile	deactivate silica gel	GC-ECD
15	NT				
16					
17					
18	NT				
19	NT				
20	NT				
21	NT				

Table 38 Sample S1 Tomato Chlorpyrifos Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	20	Solid-Liquid	DCM,Hex		GCMS & LCMS
2	10	QuEChERS	Acetonitrile	150 mg PSA, 900mg MgSO4	GC-FPD
3	10	QuEChERS	ACN	d-SPE	GC-MS/MS
4	10	QuEChERS	Acetonitrile	PSA	GC-MS/MS
5	10	QuEChERS	Acetonitrile	Florisil	GC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	GC-MS/MS
7	15	Liquid-Liquid	Acetonitrile	dSPE	GC-MS/MS
8	10	QuEChERS	ACETONITRILE	PSA	GC-FPD
9	5	QuEChERS	Acetonitrile	Dispersive SPE:- PSA, C18, MgSO4.	GC-MS/MS
10	20	QuEChERS	Acetonitrile	DSPE	GC-FPD
11	3	Solid-Liquid	Acidified Ethyl Acetate	PSA	LC-MS/MS
12	15	QuEChERS	ACN	PSA	LC-MS/MS
13	NT				
14	20	QuEChERS	Acetonitrile	deactivate silica gel	GC-ECD
15	NT				
16	10	Solid-Liquid	Acetonitrile	C-18,CARBON, FLORISIL	GC-FPD
17					
18	10	Solid-Liquid	Acetonitrile	C18, carbon, florisil	GC-NPD
19	10	QuEChERS	Acetonitrile	Dispersive SPE	GC-MS
20	10	QuEChERS	Acetonitrile	Dispersive SPE	LC-MS/MS
21	10	SPE	acetonitrile	C18,Envicarb,Florisil	GC-NPD

Table 39 Sample S1 Tomato Endosulfan Sulfate Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	20	Solid-Liquid	DCM,Hex		GC-MS/MS
2	10	QuEChERS	Acetonitrile	150 mg PSA, 900mg MgSO4	GC-ECD
3	10	QuEChERS	ACN	d-SPE	GC-MS/MS
4	10	QuEChERS	Acetonitrile	PSA	GC-MS/MS
5	10	QuEChERS	Acetonitrile	Florisil	GC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	GC-MS/MS
7	15	Liquid-Liquid	Acetonitrile	dSPE	GC-MS/MS
8	10	QuEChERS	ACETONITRILE	PSA	GC-ECD
9	5	QuEChERS	Acetonitrile	Dispersive SPE:- PSA, C18, MgSO4.	GC-MS/MS
10	20	QuEChERS	Acetonitrile	DSPE	GC-ECD
11	3	Solid-Liquid	Acidified Ethyl Acetate	PSA	GC-MS/MS
12	NT				
13	NT				
14	20	QuEChERS	Acetonitrile	deactivate silica gel	GC-ECD
15	NT				
16	10	Solid-Liquid	Acetonitrile	C-18,Carbon,Florisil	GC-ECD
17					
18	10	Solid-Liquid	Acetonitrile	C18, carbon, florisil	GC-ECD
19	10	QuEChERS	Acetonitrile	Dispersive SPE	GC-MS
20	10	QuEChERS	Acetonitrile	Dispersive SPE	GC-MS/MS
21	10	SPE	acetonitrile	C18,Envicarb,Florisil	GC-ECD

Table 40 Sample S1 Tomato Fenhexamid Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	20	Solid-Liquid	DCM,Hex		GCMS & LCMS
2	NT				
3	10	QuEChERS	ACN	d-SPE	LC-MS/MS
4	10	QuEChERS	Acetonitrile		LC-MS/MS
5	10	QuEChERS	Acetonitrile	PSA	LC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	GC-MS/MS
7	15	Liquid-Liquid	Acetonitrile	dSPE	LC-MS/MS
8	NT				
9	5	QuEChERS	Acetonitrile	Dispersive SPE:- PSA, C18, MgSO4.	LC-MS/MS
10	NT				
11	3	Solid-Liquid	Acidified Ethyl Acetate	PSA	LC-MS/MS
12	15	QuEChERS	ACN	PSA	LC-MS/MS
13	NT				
14	NT				
15	NT				
16	NT				
17					
18	NT				
19	NT				
20	NT				
21	NT				

Table 41 Sample S2 Bok Choy Bifenthrin Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	20	Solid-Liquid	DCM,Hex		GC-MS/MS
2	10	QuEChERS	Acetonitrile	150 mg PSA,45 mg GCB and 855 mg MgSO4	GC-ECD
3	10	QuEChERS	ACN	d-SPE	GC-MS/MS
4	10	QuEChERS	Acetonitrile	PSA	GC-MS/MS
5	10	QuEChERS	Acetonitrile	Florisil	GC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	GC-MS/MS
7	15	Liquid-Liquid	Acetonitrile	dSPE	GC-MS/MS
8	NT				
9	5	QuEChERS	Acetonitrile	Dispersive SPE:- PSA, C18, MgSO4.	GC-MS/MS
10	20	QuEChERS	Acetonitrile	DSPE	GC-ECD
11	3	Solid-Liquid	Acidified Ethyl Acetate	PSA	GC-MS/MS
12					
13	NT				
14	20	QuEChERS	Acetonitrile	deactivate silica gel	GC-ECD
15	10	Solid-Liquid	ethylacetate	QuEChERS	GCMSMS and LCMSMS
16	10	Solid-Liquid	ACN	C-18,CARBON, FLORISIL	GC-MS/MS
17					
18	10	Solid-Liquid	Acetonitrile	C18, carbon, florisil	GC-ECD
19	10	QuEChERS	Acetonitrile	Dispersive SPE	GC-MS
20	10	QuEChERS	Acetonitrile	Dispersive SPE	GC-MS/MS
21	10	SPE	acetonitrile	C18,Envicarb,Florisil	GC-ECD

Table 42 Sample S2 Bok Choy Indoxacarb Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	20	Solid-Liquid	DCM,Hex		GCMS & LCMS
2	NT				
3	NT				
4	10	QuEChERS	Acetonitrile		LC-MS/MS
5	10	QuEChERS	Acetonitrile	PSA	LC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	GC-MS/MS
7	15	Liquid-Liquid	Acetonitrile	dSPE	LC-MS/MS
8	NT				
9	5	QuEChERS	Acetonitrile	Dispersive SPE:- PSA, C18, MgSO4.	LC-MS/MS
10	NT				
11	3	Solid-Liquid	Acidified Ethyl Acetate	PSA	LC-MS/MS
12					
13	NT				
14	NT				
15	10	Solid-Liquid	ethylacetate	QuEChERS	GCMSMS and LCMSMS
16	10	Solid-Liquid	ACN	C-18,CARBON, FLORISIL	GC-MS/MS
17					
18	10	Solid-Liquid	Acetonitrile	C18, carbon, florisil	GC-ECD
19	NT				
20	10	QuEChERS	Acetonitrile	Dispersive SPE	LC-MS/MS
21	NT				

Table 43 Sample S2 Bok Choy Iprodione Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	20	Solid-Liquid	DCM,Hex		GCMS & LCMS
2	10	QuEChERS	Acetonitrile	150 mg PSA,45 mg GCB and 855 mg MgSO4	GC-ECD
3	10	QuEChERS	ACN	d-SPE	GC-MS/MS
4	10	QuEChERS	Acetonitrile	PSA	GC-MS/MS
5	10	QuEChERS	Acetonitrile	Florisil	GC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	GC-MS/MS
7	NT				
8	NT				
9	5	QuEChERS	Acetonitrile	Dispersive SPE:- PSA, C18, MgSO4.	GC-MS/MS
10	NT				
11	3	Solid-Liquid	Acidified Ethyl Acetate	PSA	LC-MS/MS
12					
13	1	Liquid-Liquid	Acetone:Hexane (2:1)	GPC / Florisil	GC-MS
14	NT				
15	10	Solid-Liquid	ethylacetate	QuEChERS	GCMSMS and LCMSMS
16	10	Solid-Liquid	ACN	C-18,CARBON, FLORISIL	GC-MS/MS
17					
18	10	Solid-Liquid	Acetonitrile	C18, carbon, florisil	GC-ECD
19	NT				
20	10	QuEChERS	Acetonitrile	Dispersive SPE	LC-MS/MS
21	NT				

Table 44 Sample S3 Grape Acetamiprid Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	20	Solid-Liquid	DCM,Hex		LC-MS/MS
2	NT				
3	10	QuEChERS	ACN	d-SPE	LC-MS/MS
4	10	QuEChERS	Acetonitrile		LC-MS/MS
5	10	QuEChERS	Acetonitrile	PSA	LC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	LC-MS/MS
7	15	Liquid-Liquid	Acetonitrile	dSPE	LC-MS/MS
8	NT				
9	5	QuEChERS	Acetonitrile	Dispersive SPE:- PSA, C18, MgSO4.	LC-MS/MS
10	NT				
11	3	Solid-Liquid	Acidified Ethyl Acetate	PSA	LC-MS/MS
12					
13	NT				
14	NT				
15	10	Solid-Liquid	ethylacetate	QuEChERS	GCMSMS and LCMSMS
16	10	Solid-Liquid	ACN	QuEChERS d-SPE	LC-MS/MS
17					
18	NT				
19	NT				
20	10	QuEChERS	Acetonitrile	Dispersive SPE	LC-MS/MS
21	NT				

Table 45 Sample S3 Grape Bifenthrin Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	20	Solid-Liquid	DCM,Hex		GC-MS/MS
2	10	QuEChERS	Acetonitrile	150 mg PSA,45 mg GCB and 855 mg MgSO4	GC-ECD
3	10	QuEChERS	ACN	d-SPE	GC-MS/MS
4	10	QuEChERS	Acetonitrile	PSA	GC-MS/MS
5	10	QuEChERS	Acetonitrile	Florisil	GC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	GC-MS/MS
7	15	Liquid-Liquid	Acetonitrile	dSPE	GC-MS/MS
8	NT				
9	5	QuEChERS	Acetonitrile	Dispersive SPE:- PSA, C18, MgSO4.	GC-MS/MS
10	20	QuEChERS	Acetonitrile	DSPE	GC-ECD
11	3	Solid-Liquid	Acidified Ethyl Acetate	PSA	GC-MS/MS
12					
13	NT				
14	20	QuEChERS	Acetonitrile	deactivate silica gel	GC-ECD
15	10	Solid-Liquid	ethylacetate	QuEChERS	GCMSMS and LCMSMS
16	10	Solid-Liquid	ACN	C-18,CARBON, FLORISIL	GC-MS/MS
17					
18	10	Solid-Liquid	Acetonitrile	C18, carbon, florisil	GC-ECD
19	10	QuEChERS	Acetonitrile	Dispersive SPE	GC-MS
20	10	QuEChERS	Acetonitrile	Dispersive SPE	GC-MS/MS
21	10	SPE	acetonitrile	C18,Envicarb,Florisil	GC-ECD

Table 46 Sample S3 Grape Chlorpyrifos Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	20	Solid-Liquid	DCM,Hex		GCMS & LCMS
2					
3	10	QuEChERS	ACN	d-SPE	GC-MS/MS
4	10	QuEChERS	Acetonitrile	PSA	GC-MS/MS
5	10	QuEChERS	Acetonitrile	Florisil	GC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	GC-MS/MS
7	15	Liquid-Liquid	Acetonitrile	dSPE	GC-MS/MS
8	NT				
9	5	QuEChERS	Acetonitrile	Dispersive SPE:- PSA, C18, MgSO4.	GC-MS/MS
10	20	QuEChERS	Acetonitrile	DSPE	GC-FPD
11	3	Solid-Liquid	Acidified Ethyl Acetate	PSA	LC-MS/MS
12					
13	NT				
14	20	QuEChERS	Acetonitrile	deactivate silica gel	GC-FPD
15	10	Solid-Liquid	ethylacetate	QuEChERS	GCMSMS and LCMSMS
16					
17					
18	10	Solid-Liquid	Acetonitrile	C18, carbon, florisil	GC-NPD
19	10	QuEChERS	Acetonitrile	Dispersive SPE	GC-MS
20	10	QuEChERS	Acetonitrile	Dispersive SPE	GC-MS/MS
21	10	SPE	acetonitrile	C18,Envicarb,Florisil	GC-NPD

Table 47 Sample S3 Grape Cyprodinil Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	20	Solid-Liquid	DCM,Hex		GCMS & LCMS
2	NT				
3	10	QuEChERS	ACN	d-SPE	LC-MS/MS
4	10	QuEChERS	Acetonitrile		LC-MS/MS
5	10	QuEChERS	Acetonitrile	PSA	LC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	GC-MS/MS
7	15	Liquid-Liquid	Acetonitrile	dSPE	LC-MS/MS
8	NT				
9	5	QuEChERS	Acetonitrile	Dispersive SPE:- PSA, C18, MgSO4.	LC-MS/MS
10	NT				
11	3	Solid-Liquid	Acidified Ethyl Acetate	PSA	LC-MS/MS
12					
13	NT				
14	NT				
15	NT				
16	NT				
17					
18	NT				
19	NT				
20	10	QuEChERS	Acetonitrile	Dispersive SPE	LC-MS/MS
21	NT				

Table 48 Sample S3 Grape Fenhexamid Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	20	Solid-Liquid	DCM,Hex		GCMS & LCMS
2	NT				
3	10	QuEChERS	ACN	d-SPE	LC-MS/MS
4	10	QuEChERS	Acetonitrile		LC-MS/MS
5	10	QuEChERS	Acetonitrile	PSA	LC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	GC-MS/MS
7	15	Liquid-Liquid	Acetonitrile	dSPE	LC-MS/MS
8	NT				
9	5	QuEChERS	Acetonitrile	Dispersive SPE:- PSA, C18, MgSO4.	LC-MS/MS
10	NT				
11	3	Solid-Liquid	Acidified Ethyl Acetate	PSA	LC-MS/MS
12					
13	NT				
14	NT				
15	10	Solid-Liquid	ethylacetate	QuEChERS	GCMSMS and LCMSMS
16	NT				
17					
18	NT				
19	NT				
20	NT				
21	NT				

Table 49 Sample S3 Grape Metalaxyl Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	20	Solid-Liquid	DCM,Hex		GCMS & LCMS
2	NT				
3	10	QuEChERS	ACN	d-SPE	LC-MS/MS
4	10	QuEChERS	Acetonitrile		LC-MS/MS
5	10	QuEChERS	Acetonitrile	PSA	LC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	GC-MS/MS
7	15	Liquid-Liquid	Acetonitrile	dSPE	GC-MS/MS
8	NT				
9	5	QuEChERS	Acetonitrile	Dispersive SPE:- PSA, C18, MgSO4.	LC-MS/MS
10	NT				
11	3	Solid-Liquid	Acidified Ethyl Acetate	PSA	LC-MS/MS
12					
13	NT				
14	NT				
15	NT				
16	NT				
17					
18	NT				
19	10	QuEChERS	Acetonitrile	Dispersive SPE	GC-MS
20	10	QuEChERS	Acetonitrile	Dispersive SPE	GC-MS/MS
21	NT				

Table 50 Sample S3 Grape Methomyl Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	20	Solid-Liquid	DCM,Hex		LC-MS/MS
2	NT				
3	10	QuEChERS	ACN	d-SPE	LC-MS/MS
4	10	QuEChERS	Acetonitrile		LC-MS/MS
5	10	QuEChERS	Acetonitrile	PSA	LC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	LC-MS/MS
7	15	Liquid-Liquid	Acetonitrile	dSPE	LC-MS/MS
8	NT				
9	5	QuEChERS	Acetonitrile	Dispersive SPE:- PSA, C18, MgSO4.	LC-MS/MS
10	NT				
11	3	Solid-Liquid	Acidified Ethyl Acetate	PSA	LC-MS/MS
12					
13	NT				
14	NT				
15	10	Solid-Liquid	ethylacetate	QuEChERS	GCMSMS and LCMSMS
16	NT				
17					
18	NT				
19	NT				
20	10	QuEChERS	Acetonitrile	Dispersive SPE	LC-MS/MS
21	NT				

Table 51 Sample S3 Grape Metrafenone Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	20	Solid-Liquid	DCM,Hex		GCMS & LCMS
2	NT				
3	NT				
4	NT				
5	10	QuEChERS	Acetonitrile	PSA	LC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	LC-MS/MS
7	NT				
8	NT				
9	5	QuEChERS	Acetonitrile	Dispersive SPE:- PSA, C18, MgSO4.	LC-MS/MS
10	NT				
11	3	Solid-Liquid	Acidified Ethyl Acetate	PSA	GC-MS/MS
12					
13	NT				
14	NT				
15	10	Solid-Liquid	ethylacetate	QuEChERS	GCMSMS and LCMSMS
16	NT				
17					
18	NT				
19	NT				
20	10	QuEChERS	Acetonitrile	Dispersive SPE	LC-MS/MS
21	NT				

Table 52 Sample S4 Coriander Chlorpyrifos Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	20	Solid-Liquid	DCM,Hex		GCMS & LCMS
2					
3	10	QuEChERS	ACN	d-SPE	GC-MS/MS
4	10	QuEChERS	Acetonitrile	PSA	GC-MS/MS
5	10	QuEChERS	Acetonitrile	Florisil	GC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	GC-MS/MS
7	15	Liquid-Liquid	Acetonitrile	dSPE	GC-MS/MS
8	NT				
9	5	QuEChERS	Acetonitrile	Dispersive SPE:- PSA, C18, MgSO4.	GC-MS/MS
10	20	QuEChERS	Acetonitrile	DSPE	GC-FPD
11	3	Solid-Liquid	Acidified Ethyl Acetate	PSA	LC-MS/MS
12					
13	NT				
14	20	QuEChERS	Acetonitrile	deactivate silica gel	GC-FPD
15	NT				
16					
17					
18	10	Solid-Liquid	Acetonitrile	C18, carbon, florisil	GC-NPD
19	10	QuEChERS	Acetonitrile	Dispersive SPE	GC-MS
20	10	QuEChERS	Acetonitrile	Dispersive SPE	LC-MS/MS
21	10	SPE	acetonitrile	C18,Envicarb,Florisil	GC-NPD

Table 53 Sample S4 Coriander Cypermethrin Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	20	Solid-Liquid	DCM,Hex		GC-MS/MS
2					
3	10	QuEChERS	ACN	d-SPE	GC-MS/MS
4	10	QuEChERS	Acetonitrile	PSA	GC-MS/MS
5	10	QuEChERS	Acetonitrile	Florisil	GC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	GC-MS/MS
7	15	Liquid-Liquid	Acetonitrile	dSPE	GC-MS/MS
8	NT				
9	5	QuEChERS	Acetonitrile	Dispersive SPE:- PSA, C18, MgSO4.	GC-MS/MS
10	20	QuEChERS	Acetonitrile	DSPE	GC-ECD
11	3	Solid-Liquid	Acidified Ethyl Acetate	PSA	GC-MS/MS
12					
13	NT				
14	20	QuEChERS	Acetonitrile	deactivate silica gel	GC-ECD
15	NT				
16					
17					
18	10	Solid-Liquid	Acetonitrile	C18, carbon, florisil	GC-ECD
19	10	QuEChERS	Acetonitrile	Dispersive SPE	GC-MS
20	10	QuEChERS	Acetonitrile	Dispersive SPE	GC-MS/MS
21	10	SPE	acetonitrile	C18,Envicarb,Florisil	GC-ECD

Table 54 Sample S4 Coriander Cyprodinil Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	20	Solid-Liquid	DCM,Hex		GCMS & LCMS
2	NT				
3	10	QuEChERS	ACN	d-SPE	LC-MS/MS
4	10	QuEChERS	Acetonitrile		LC-MS/MS
5	10	QuEChERS	Acetonitrile	PSA	LC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	GC-MS/MS
7	15	Liquid-Liquid	Acetonitrile	dSPE	LC-MS/MS
8	NT				
9	5	QuEChERS	Acetonitrile	Dispersive SPE:- PSA, C18, MgSO4.	LC-MS/MS
10	NT				
11	3	Solid-Liquid	Acidified Ethyl Acetate	PSA	LC-MS/MS
12					
13	NT				
14	NT				
15	NT				
16	NT				
17					
18	NT				
19	NT				
20	10	QuEChERS	Acetonitrile	Dispersive SPE	LC-MS/MS
21	NT				

Table 55 Sample S4 Coriander Fipronil Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	20	Solid-Liquid	DCM,Hex		GC-MS/MS
2	10	QuEChERS	Acetonitrile	150 mg PSA,45 mg GCB and 855 mg MgSO4	GC-ECD
3	10	QuEChERS	ACN	d-SPE	GC-MS/MS
4	10	QuEChERS	Acetonitrile		LC-MS/MS
5	10	QuEChERS	Acetonitrile	PSA	LC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	GC-MS/MS
7	15	Liquid-Liquid	Acetonitrile	dSPE	LC-MS/MS
8	10	QuEChERS	ACETONITRILE	PSA	GC-ECD
9	5	QuEChERS	Acetonitrile	Dispersive SPE:- PSA, C18, MgSO4.	LC-MS/MS
10	NT				
11	3	Solid-Liquid	Acidified Ethyl Acetate	PSA	GC-MS/MS
12	NT				
13	NT				
14	NT				
15	NT				
16	10	Solid-Liquid	ACN	C-18,CARBON, FLORISIL	GC-MS/MS
17					
18	10	Solid-Liquid	Acetonitrile	C18, carbon, florisil	GC-ECD
19	10	QuEChERS	Acetonitrile	Dispersive SPE	GC-MS
20	10	QuEChERS	Acetonitrile	Dispersive SPE	LC-MS/MS
21	10	SPE	acetonitrile	C18,Envicarb,Florisil	GC-ECD

Table 56 Sample S4 Coriander Iprodione Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1					
2					
3	10	QuEChERS	ACN	d-SPE	GC-MS/MS
4	10	QuEChERS	Acetonitrile	PSA	GC-MS/MS
5	10	QuEChERS	Acetonitrile	Florisil	GC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	GC-MS/MS
7	NT				
8	NT				
9	5	QuEChERS	Acetonitrile	Dispersive SPE:- PSA, C18, MgSO4.	GC-MS/MS
10	NT				
11	3	Solid-Liquid	Acidified Ethyl Acetate	PSA	LC-MS/MS
12					
13	1	Liquid-Liquid	Acetone:Hexane (2:1)	GPC / Florisil	GC-MS
14	NT				
15	NT				
16	10	Solid-Liquid	ACN	C-18,CARBON, FLORISIL	GC-MS/MS
17					
18	10	Solid-Liquid	Acetonitrile	C18, carbon, florisil	GC-ECD
19	NT				
20	10	QuEChERS	Acetonitrile	Dispersive SPE	LC-MS/MS
21	NT				

Table 57 Sample S4 Coriander Linuron Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	20	Solid-Liquid	DCM,Hex		LC-MS/MS
2	NT				
3	10	QuEChERS	ACN	d-SPE	LC-MS/MS
4	10	QuEChERS	Acetonitrile		LC-MS/MS
5	10	QuEChERS	Acetonitrile	PSA	LC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	LC-MS/MS
7	15	Liquid-Liquid	Acetonitrile	dSPE	LC-MS/MS
8	NT				
9	5	QuEChERS	Acetonitrile	Dispersive SPE:- PSA, C18, MgSO4.	LC-MS/MS
10	NT				
11	3	Solid-Liquid	Acidified Ethyl Acetate	PSA	LC-MS/MS
12	NT				
13	1	Liquid-Liquid	Acetone:Hexane (2:1)	GPC / Florisil	GC-MS
14	NT				
15	NT				
16	NT				
17					
18	NT				
19	NT				
20	10	QuEChERS	Acetonitrile	Dispersive SPE	LC-MS/MS
21	NT				

Table 58 Sample S4 Coriander Permethrin Methodology

Lab. Code	Sample Mass for Analysis (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	20	Solid-Liquid	DCM,Hex		GC-MS/MS
2	10	QuEChERS	Acetonitrile	150 mg PSA,45 mg GCB and 855 mg MgSO4	GC-ECD
3	10	QuEChERS	ACN	d-SPE	GC-MS/MS
4	10	QuEChERS	Acetonitrile	PSA	GC-MS/MS
5	10	QuEChERS	Acetonitrile	Florisil	GC-MS/MS
6	5	QUECHER	Acetonitrile	PSA	GC-MS/MS
7	15	Liquid-Liquid	Acetonitrile	dSPE	GC-MS/MS
8	NT				
9	5	QuEChERS	Acetonitrile	Dispersive SPE:- PSA, C18, MgSO4.	GC-MS/MS
10	20	QuEChERS	Acetonitrile	DSPE	GC-ECD
11	NT				
12	NT				
13	NT				
14	NT				
15	NT				
16					
17					
18	10	Solid-Liquid	Acetonitrile	C18, carbon, florisil	GC-ECD
19	10	QuEChERS	Acetonitrile	Dispersive SPE	GC-MS
20	10	QuEChERS	Acetonitrile	Dispersive SPE	GC-MS/MS
21	10	SPE	acetonitrile	C18,Envicarb,Florisil	GC-ECD

APPENDIX 5 ACRONYMS AND ABBREVIATIONS

2,4-D	2,4-Dichlorophenoxyacetic acid
ACE	Acetone
ACN	Acetonitrile
AV	Assigned Value
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
DCM	Dichloromethane
dSPE	Dispersive Solid Phase Extraction
ECD	Electron Capture Detection
EtOAc	Ethyl Acetate
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
Min	Minimum
MRL	Maximum Residue Limit
MS	Mass Spectrometry
MS/MS	Tandem Mass Spectrometry
MU	Measurement Uncertainty
N	Number of numeric results
NATA	National Association of Testing Authorities, Australia
NMI	National Measurement Institute, Australia

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

END OF REPORT