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National Measurement Institute

Proficiency Test Final Report
AQA 26-10
Pesticides in Potable Water

August 2026

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SUMMARY

This report presents the results of the proficiency testing study AQA 26-10 Pesticides in Potable Water.

The sample set consisted of 3 potable water samples. Samples were prepared by spiking potable water with various pesticides.

Of a possible 474 results, 241 numeric results (51%) were submitted. Thirty-five results were a 'less than' value (< *x*) or Not Reported (NR), and 198 results were Not Tested (NT).

The assigned values for all scored analytes were the robust averages of participants' results. The associated uncertainties were evaluated from the robust standard deviations of the participants' results. The consensus of participants' results is not traceable to any external reference, so although expressed in SI units, metrological traceability has not been established.

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

i. Assess participants' ability to correctly identify pesticides in potable water.

Laboratories 6, 10, and 12 reported numeric results for all fourteen scored analytes in this study.

Laboratories 2, 5, 7, 9, 10, 11, 14, 15, 16, and 17 did not report numeric results for analytes that they tested for and were present in the test samples (total of 14 results).

Three participants reported analytes that were not spiked into the test samples (total of 3 results).

ii. Compare participants' performance and assess their capabilities to measure pesticides in potable water.

Of 139 z-scores, 122 (88%) returned a score of $|z| \leq 2.0$, indicating an acceptable performance.

Of 137 E_n-scores, 112 (82%) returned a score of $|E_n| < 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratory 6 achieved acceptable z-scores and E_n-scores across all 14 scored analytes.

iii. Assess the consequence of participants' results for pesticides in potable water against regulatory guidelines.

Of 113 results assessed against the Australian Drinking Water Guidelines, 102 (90%) correctly reflected whether the sample exceeded the guideline or not.

In some cases, reported results had measurement uncertainties spanning the guideline level. This may lead to an inconclusive assessment even when the assigned value indicates compliance or non-compliance. These participants may need to review if their measurement uncertainties are too large to be fit-for-purpose.

iv. Evaluate participants' methods for the measurement of pesticides in potable water.

Participants used a wide variety of methods. The most common methodology used in this study was liquid-liquid extraction with dichloromethane, followed by analysis using GC-MS(/MS).

Both GC and LC techniques were used, depending on the analyte.

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

Of 241 numeric results, 240 were reported with an expanded measurement uncertainty. The magnitude of reported uncertainties was within the range of 2.6% to 100%. Participants used a wide variety of procedures to evaluate their uncertainty.

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

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

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1 INTRODUCTION

1.1 NMIA Proficiency Testing Program

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

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

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

1.2 Study Aims

The aims of the study were to:

- assess participants' ability to correctly identify pesticides in potable water;
- compare participants' performance and assess their capabilities to measure pesticides in potable water;
- assess the consequence of participants' results for pesticides in potable water against regulatory guidelines;
- evaluate participants' methods for the measurement of pesticides in potable water;
- develop the practical application of measurement uncertainty, and provide participants with information that will be useful in assessing their uncertainty evaluations; and
- produce materials that can be used in method validation and as control samples.

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

1.3 Study Conduct

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

NMIA is accredited by the National Association of Testing Authorities, Australia (NATA) to ISO/IEC 17043 as a provider of proficiency testing schemes.[1] This study falls within the scope of NMIA's accreditation (Accreditation No. 198; Site No. 14485).

2 STUDY INFORMATION

2.1 Study Timetable

The timetable of the study was:

Invitations sent 13/04/2026

Samples sent 11/05/2026

Results due 15/06/2026

Interim Report 17/06/2026

Preliminary Report 22/06/2026

2.2 Participation and Laboratory Code

Twenty laboratories registered to participate in this study. One laboratory requested 2 sets of samples to be analysed independently, for a total of 21 participants. All participants were assigned a confidential laboratory code number for this study. Twenty participants submitted results.

2.3 Selection of Analytes and Test Material Preparation

When selecting analytes and spiking values for this study, consideration was given to:

- the Australian Drinking Water Guidelines (ADWG);[5]
- a variety of analytes amenable to gas and/or liquid chromatography; and
- feedback from participants and other stakeholders.

Three test samples were prepared by adding pesticide standard solutions to potable water. The spiked values for the samples and corresponding ADWG values are presented in Table 1.[5]

Table 1 Spiked Values of Test Samples

Sample	Analyte	Spiked Value (mg/L)	ADWG Health Guideline Value[5] (mg/L)
S1	Atrazine	0.0151	0.02
S1	Azinphos-methyl	0.0400	0.03
S1	cis-Chlordane*	0.000985	0.002
S1	trans-Chlordane*	0.000983	0.002
S1	α-Cypermethrin*	0.401	0.2
S1	p,p'-DDT	0.00824	0.009**
S1	Dieldrin	0.000352	0.0003***
S1	α-Endosulfan*	0.0300	0.02
S1	Maldison	0.151	0.07
S1	Picloram	0.604	0.3
S1	Pirimiphos-methyl	0.152	0.09
S1	Total Propiconazole****	0.181	0.1
S2	Acephate	0.00991	0.008
S2	Atrazine	0.0251	0.02
S2	Bromacil	0.650	0.4

Sample	Analyte	Spiked Value (mg/L)	ADWG Health Guideline Value[5] (mg/L)
S2	2,4-D	0.0402	0.03
S2	Fipronil	0.00147	0.0007
S2	MCPA	0.0398	0.04
S2	Total Metolachlor****	0.602	0.3
S2	Metsulfuron-methyl	0.0607	0.04
S2	Picloram	1.20	0.3
S2	Pirimicarb	0.00649	0.007
S2	Triadimefon	0.0900	0.09
S3	AMPA	0.0100	-
S3	Glyphosate	0.0914	1

*Participants were requested to report for total chlordane, cypermethrin, and endosulfan. The ADWG does not differentiate between isomers of these compounds. **The ADWG value is for DDT. Participants were requested to report for only p,p'-DDT. ***The ADWG value is for aldrin and dieldrin combined. Participants were requested to report for aldrin and dieldrin separately. ****The samples were spiked with standards containing mixtures of propiconazole and metolachlor isomers. The ADWG does not differentiate between isomers of these compounds.

Additional sample preparation details are provided in Appendix 1.

2.4 Homogeneity and Stability of Test Materials

No homogeneity or stability testing was conducted for this study. The samples were prepared, packaged, stored, and dispatched using a process that has been demonstrated to produce sufficiently homogeneous and stable samples in previous NMIA PT studies.

To further assess possible instability, the results returned by participants were compared to the spiked concentrations. For scored analytes, assigned values were within the range of 54% to 106% of the spiked values. This is similar to ratios observed in previous NMIA PT studies.

The results of this study also gave no reason to question the homogeneity or stability of the samples (Appendix 2).

2.5 Test Material Storage, Dispatch, and Receipt

After preparation, the samples were stored at 4 °C. Samples were packaged into insulated polystyrene foam boxes with cooler bricks and dispatched by courier on 11 May 2026.

The following items were packaged with the samples:

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

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

2.6 Instructions to Participants

Participants were provided with a list of potential analytes spiked into Samples S1 and S2 (Tables 2 and 3) and were informed that Sample S3 was spiked with AMPA and glyphosate.

Table 2 List of Possible Analytes for Sample S1

Aldrin	p,p'-DDT	Fenthion	Piperonyl butoxide
Atrazine	Deltamethrin	Heptachlor	Pirimiphos-ethyl
Azinphos-methyl	Diazinon	Maldison (Malathion)	Pirimiphos-methyl
Chlordane (total)	Dichlorvos	Parathion	Propargite
Chlorfenvinphos	Dieldrin	Parathion-methyl	Propiconazole (total)
Chlorpyrifos	Dimethoate	Pendimethalin	Simazine
Cyfluthrin (total)	Endosulfan (total)	Permethrin (total)	Tetrachlorvinphos
Cypermethrin (total)	Ethion	Picloram	

Table 3 List of Possible Analytes for Sample S2

Acephate	2,4-D	Metolachlor (total)	2,4,5-T
Aldicarb	Dicamba	Metsulfuron-methyl	Triadimefon
Atrazine	Diuron	Omethoate	Trichlopyr
Bromacil	Fipronil	Picloram	
Carbendazim	MCPA	Pirimicarb	
Clopyralid	Methomyl	Propazine	

Participants were instructed as follows:

- If samples cannot be analysed on the day of receipt, please store them refrigerated.
- Quantitatively analyse the samples using your routine test method.
- Participants need not test for all listed analytes.
- For each analyte in each sample, report a single result in units of mg/L. This figure will be used in all statistical analysis in the study report.
- Report results as you would report to a client, i.e. corrected for recovery or not according to your standard procedure and applying the limit of reporting of the method used for analysis (no limit of reporting has been set for this study).
- For each analyte in each sample, report the associated expanded uncertainty in units of mg/L (e.g. 0.05 ± 0.02 mg/L).
- If determined, report your percentage recovery. This will be presented in the report for information only.
- Report any listed analyte not tested as NT as the result.
- Report the basis of your uncertainty evaluation as requested in the results sheet (e.g. uncertainty budget, repeatability precision, long term result variability).
- Please complete the method details as requested in the Methodology sheet.
- Return the completed results sheet by email (proficiency@measurement.gov.au).
- Please return results by 5 June 2026. Late results may not be included in the study report.

The results due date was later extended to 12 June 2026 for all participants due to a circumstance affecting a participant.

2.7 Interim Report and Preliminary Report

An Interim Report was emailed to all participants on 17 June 2026.

A Preliminary Report was emailed to all participants on 22 June 2026. This report included a summary of the results reported by participants, assigned values, performance coefficients of variation, 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 Participants' Test Methods

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

3.2 Basis of Participants' Measurement Uncertainty Evaluations

Participants were requested to provide information about the basis of their measurement uncertainty (MU) evaluations. Responses are presented in Tables 4 and 5. Some responses may be modified so that the participant cannot be identified.

Table 4 Basis of Measurement Uncertainty Evaluation

Lab. Code	Approach to Evaluating MU	Information Sources for MU Evaluation*		Guide Document for Evaluating MU
		Precision	Method Bias	
1**	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS	
2	Top Down - precision and evaluation of the method and laboratory bias Coverage factor not reported	Control samples - CRM Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
3	Top Down - precision and evaluation of the method and laboratory bias Coverage factor not reported	Duplicate analysis	Instrument calibration	ISO/GUM
4	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples - RM / Ex PT Sample Duplicate analysis	CRM Instrument calibration Recoveries of SS	NMIA Uncertainty Course
5	Bottom Up (ISO/GUM, fish bone/cause and effect diagram) k = 2	Control samples - SS	Recoveries of SS	ISO/GUM
6	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples - SS Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS Standard purity	Eurachem/CITAC Guide
7	Top Down - precision and evaluation of the method and laboratory bias Coverage factor not reported	Control samples - SS Duplicate analysis	CRM	ISO/GUM
9	Repeatability precision - based upon internal historical data Coverage factor not reported	Control samples - CRM		
10	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples - SS Duplicate analysis	CRM	NMIA Uncertainty Course

Lab. Code	Approach to Evaluating MU	Information Sources for MU Evaluation*		Guide Document for Evaluating MU
		Precision	Method Bias	
11	Standard deviation of replicate analyses multiplied by 2 or 3 k = 2	Duplicate analysis Instrument calibration	Instrument calibration Standard purity	Eurachem/CITAC Guide
12	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples - SS Instrument calibration	Instrument calibration Recoveries of SS Standard purity	Eurachem/CITAC Guide
13	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide
14	Top Down - precision and evaluation of the method and laboratory bias k = 2	Control samples - CRM Duplicate analysis Instrument calibration	CRM Instrument calibration	Eurachem/CITAC Guide
15	Top Down - precision and evaluation of the method and laboratory bias k = 2	Duplicate analysis Instrument calibration		NMIA Uncertainty Course
16	Coverage factor not reported	Control samples - CRM Duplicate analysis		Eurachem/CITAC Guide
17	Standard deviation of replicate analyses multiplied by 2 or 3 Coverage factor not reported	Duplicate analysis	Recoveries of SS	
18	Top Down - reproducibility (standard deviation) from PT studies used directly Coverage factor not reported	Duplicate analysis	Instrument calibration	
19	Top Down - precision and evaluation of the method and laboratory bias Coverage factor not reported	Control samples	CRM	Eurachem/CITAC Guide
20	Top Down - precision and evaluation of the method and laboratory bias k = 2	Duplicate analysis Instrument calibration	Recoveries of SS	Eurachem/CITAC Guide
21	Top Down - precision and evaluation of the method and laboratory bias Coverage factor not reported	Control samples - CRM Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	Eurachem/CITAC Guide

*SS = Spiked Samples, RM = Reference Material, CRM = Certified Reference Material. **Additional information presented in Table 5.

Table 5 Basis of Measurement Uncertainty Evaluation – Additional Information

Lab. Code	Measurement Uncertainty Evaluation Additional Information
1	Uncertainty estimated as bias + 2SD based on method performance

3.3 Participants' Comments

Participants were invited to make comments or suggestions on the samples, this study, or possible future studies. Such feedback may be useful in improving future studies. Participants' comments received are presented in Table 6. Some responses may be modified so that the participant cannot be identified.

Table 6 Participants' Comments

Lab. Code	Participant's Comments	Study Coordinator's Response
13	Can we report the results as ug/L in future studies?	Thank you for your feedback. We have requested participants to report results in units of mg/L to align with the ADWG values.[5]

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 7 to 31 with summary statistics and other estimates of analyte concentration. Bar charts of results and performance scores are presented in Figures 2 to 26. An example chart with interpretation guide is shown in Figure 1.

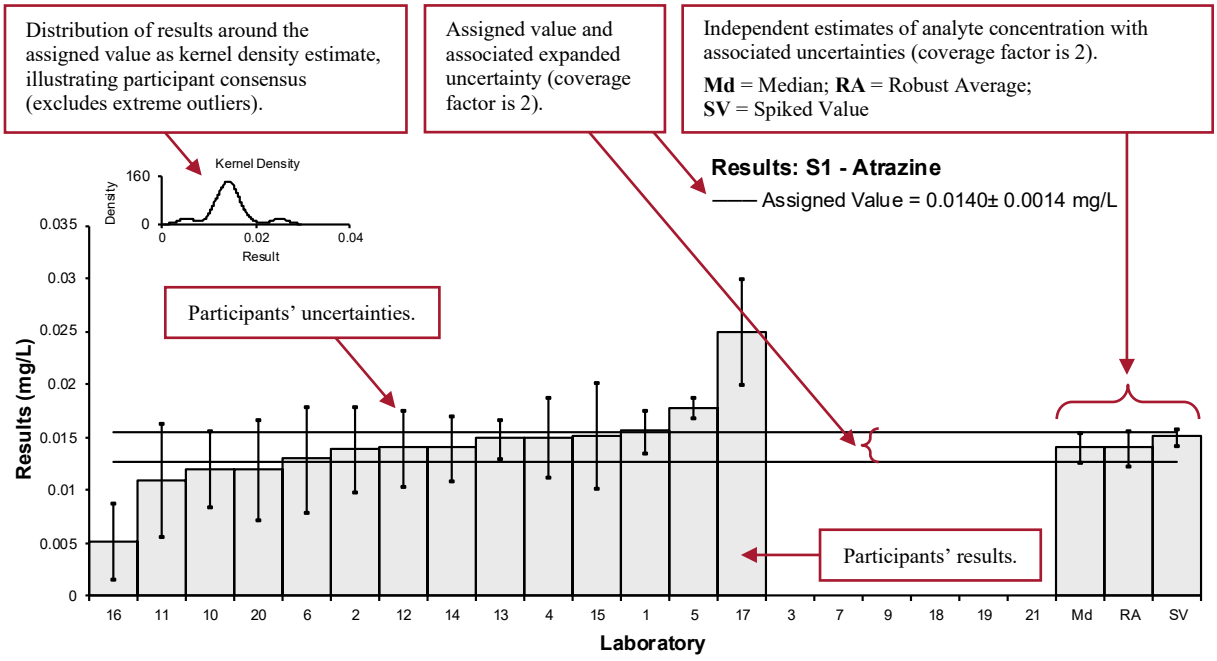


Figure 1 Guide to Presentation of Results

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

4.3 Assigned Value

The assigned value is defined as the 'value attributed to a particular property or characteristic of a proficiency testing item'.[1] In this PT study, this property is the analyte concentration in the sample. Assigned values were the robust averages of participants' results with all outliers removed, and the expanded uncertainties were evaluated from the associated robust standard deviations (robust SDs) (Appendix 3).[3,6]

4.4 Robust Average and Robust Between-Laboratory Coefficient of Variation

The robust averages and associated expanded MUs, and robust coefficients of variation (robust CVs, a measure of the variability of participants' results) were calculated as described in ISO 13528.[6] The robust CVs as presented in the Section 5 statistics tables are the robust between-laboratory CVs including outliers but excluding extreme outliers. Everywhere else in the report, the robust between-laboratory CV refers to the robust CV calculated with both outliers and extreme outliers removed.

4.5 Performance Coefficient of Variation

The performance coefficient of variation (PCV) is a set measure of the between-laboratory variation that in the judgement of the study coordinator would be expected from participants given the analyte levels present. The PCV is not the CV of participants' results. It is set by the

study coordinator and is based on the analyte concentrations and experience from previous studies. It is supported by mathematical models such as the Thompson-Horwitz equation.[7] By setting a realistic value for the PCV, a participant's performance does not depend on other participants' performances and can be compared from study to study when the PCV remains the same.

4.6 Standard Deviation for Proficiency Assessment

The standard deviation for proficiency assessment (SDPA, 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 SDPA from Equation 1

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

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

4.8 E_n-Score

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

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

where:

E_n is E_n-score

χ is a participant's result

X is the assigned value

U_χ is the expanded uncertainty of the participant's result

U_X is the expanded uncertainty of the assigned value

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

4.9 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC 17025 must establish and demonstrate the traceability and MU associated with their test results.[8]

Guidelines for quantifying uncertainty in analytical measurement are described in the Eurachem/CITAC Guide.[9]

5 TABLES AND FIGURES

Table 7

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	Atrazine
Unit	mg/L

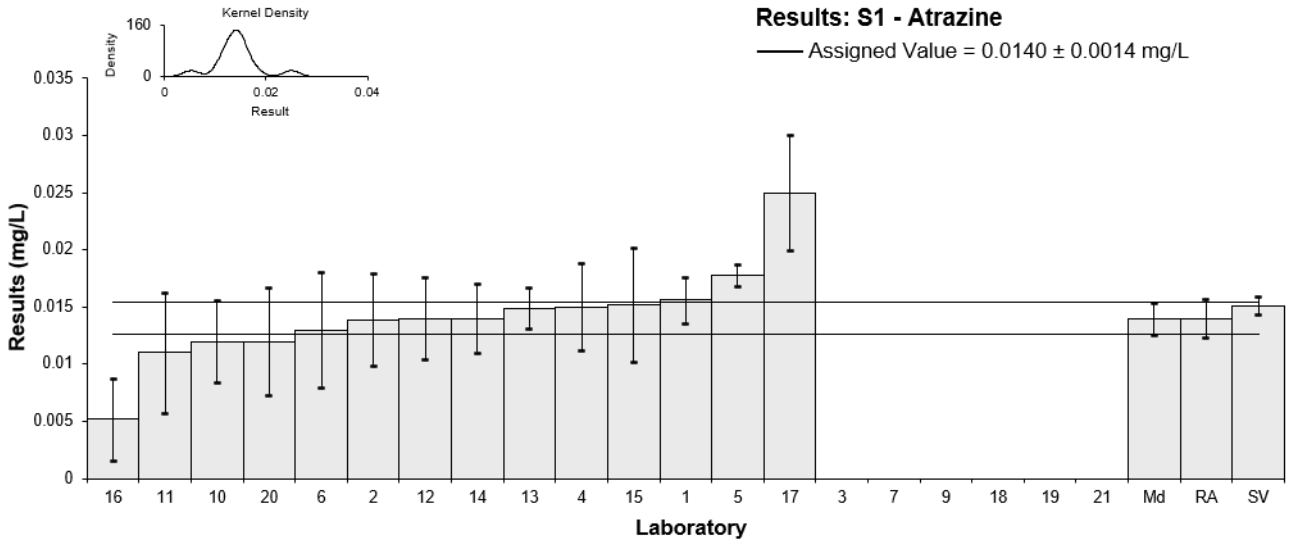
Participant Results

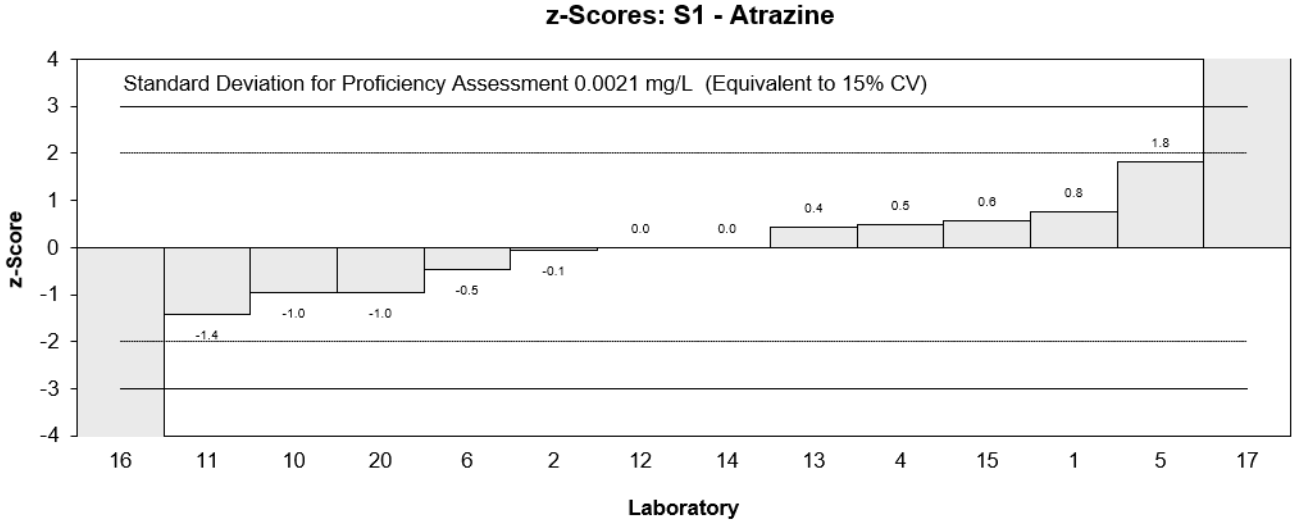
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.0156	0.002	NR	0.76	0.66
2	0.0139	0.004	NR	-0.05	-0.02
3	NT	NT	NT		
4	0.015	0.0038	108	0.48	0.25
5	0.0178	0.00096	102.05	1.81	2.24
6	0.013	0.005	NR	-0.48	-0.19
7	NT	NT	NT		
9	NT	NT	NT		
10	0.012	0.0036	NR	-0.95	-0.52
11	0.011	0.0053	NR	-1.43	-0.55
12	0.014	0.0036	96	0.00	0.00
13	0.0149	0.0018	NR	0.43	0.39
14	0.014	0.003	85.2	0.00	0.00
15	0.0152	0.005	NR	0.57	0.23
16*	0.0052	0.0036	NR	-4.19	-2.28
17*	0.025	0.005	NR	5.24	2.12
18	NT	NT	NT		
19	NT	NT	NT		
20	0.012	0.0047	NR	-0.95	-0.41
21	NT	NT	NT		

* Outlier, see Section 4.2

Statistics

Assigned Value	0.0140	0.0014
Spike Value	0.0151	0.0008
Robust Average	0.0140	0.0017
Median	0.0140	0.0014
Mean	0.0142	
N	14	
Max	0.025	
Min	0.0052	
Robust SD	0.0026	
Robust CV	19%	


Kernel Density
Density
160
0
0
0.02
0.04
Result
Results: S1 - Atrazine
Assigned Value = 0.0140 ± 0.0014 mg/L
Results (mg/L)
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
16 11 10 20 6 2 12 14 13 4 15 1 5 17 3 7 9 18 19 21 Md RA SV
Laboratory


z-Scores: S1 - Atrazine
Standard Deviation for Proficiency Assessment 0.0021 mg/L (Equivalent to 15% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
1.8
0.8
0.6
0.5
0.4
0.0
0.0
-0.1
-0.5
-1.0
-1.0
-1.4
16 11 10 20 6 2 12 14 13 4 15 1 5 17
Laboratory

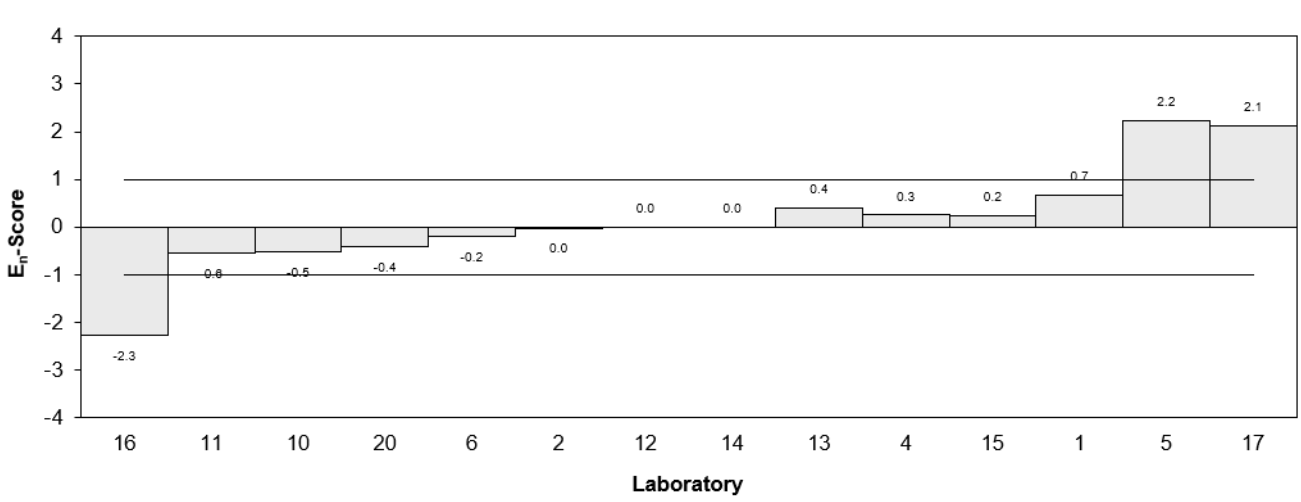

En-Scores: S1 - Atrazine
En-Score
4
3
2
1
0
-1
-2
-3
-4
2.2
2.1
0.7
0.4
0.3
0.2
0.0
0.0
0.0
-0.2
-0.4
-0.5
-0.6
-2.3
16 11 10 20 6 2 12 14 13 4 15 1 5 17
Laboratory

Figure 2

Table 8

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	Azinphos-methyl
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	0.0256	0.008	NR
2	0.2205	0.066	NR
3	0.026	0.00078	NR
4	NT	NT	NT
5	0.0176	0.00092	100.7
6	0.023	0.007	NR
7	0.023	0.0069	30
9	NT	NT	NT
10	0.022	0.0066	NR
11	0.0147	0.0027	NR
12	0.033	0.009	95
13	0.0437	0.0074	NR
14	0.0337	0.0106	79.4
15	0.029	0.009	NR
16	0.0141	0.0141	NR
17	0.038	0.011	NR
18	NT	NT	NT
19	0.029	0.0087	NR
20	0.011	0.0043	NR
21	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	0.0400	0.0020
Robust Average	0.0267	0.0070
Median	0.0258	0.0070
Mean	0.038	
N	16	
Max	0.2205	
Min	0.011	
Robust SD	0.011	
Robust CV	42%	

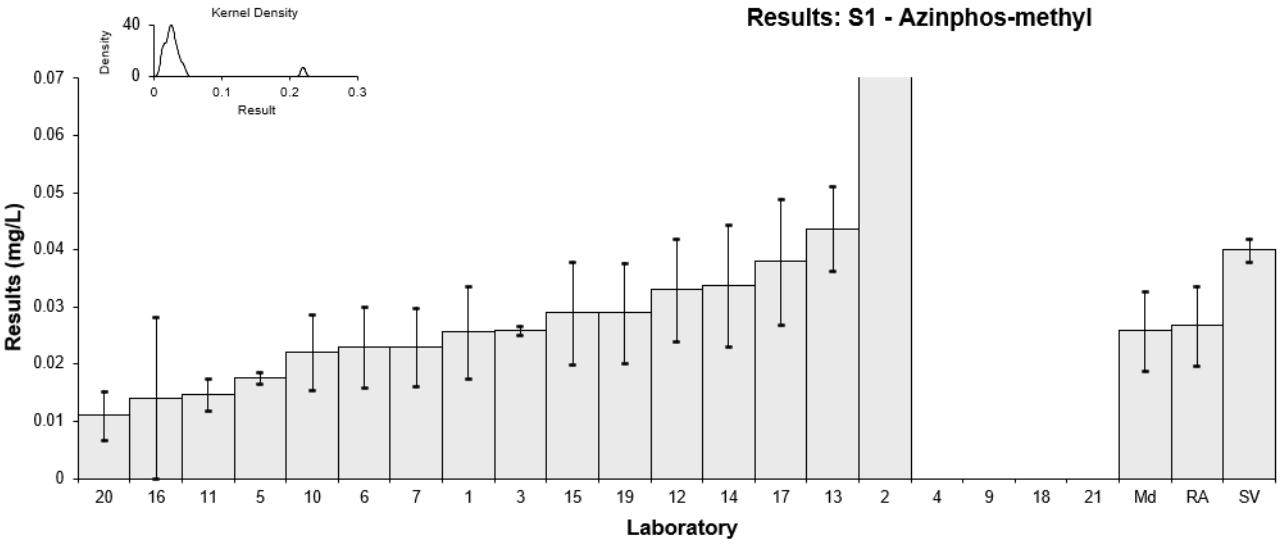

Results: S1 - Azinphos-methyl
Kernel Density
Density
40
0
0
0.1
0.2
0.3
Result
Results (mg/L)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
20
16
11
5
10
6
7
1
3
15
19
12
14
17
13
2
4
9
18
21
Md
RA
SV
Laboratory

Figure 3

Table 9

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	Total Chlordane
Unit	mg/L

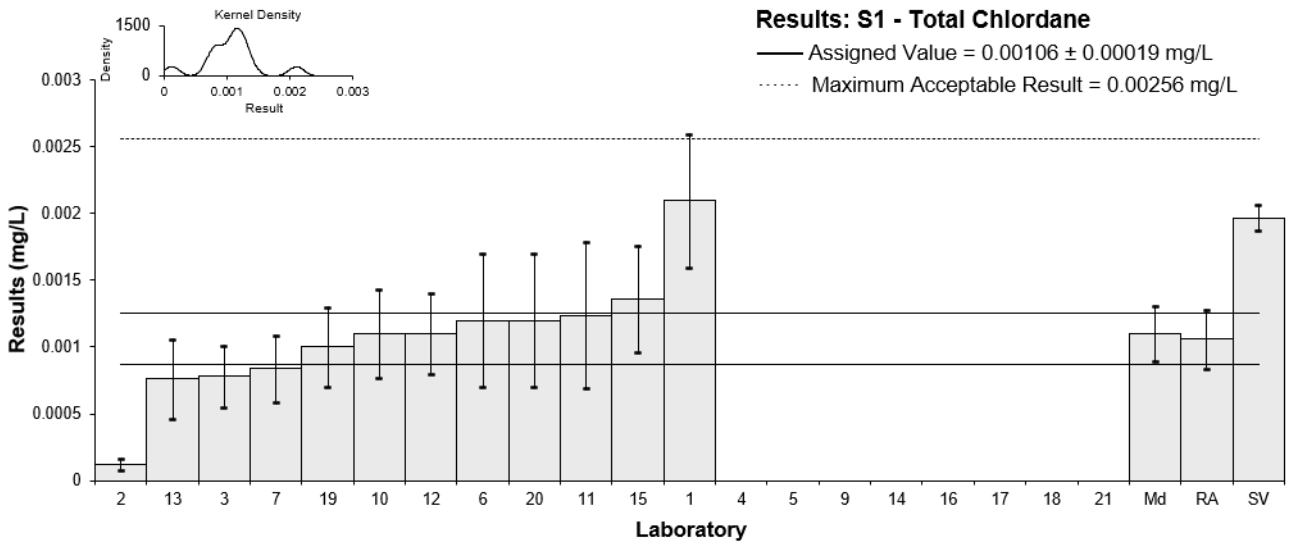
Participant Results

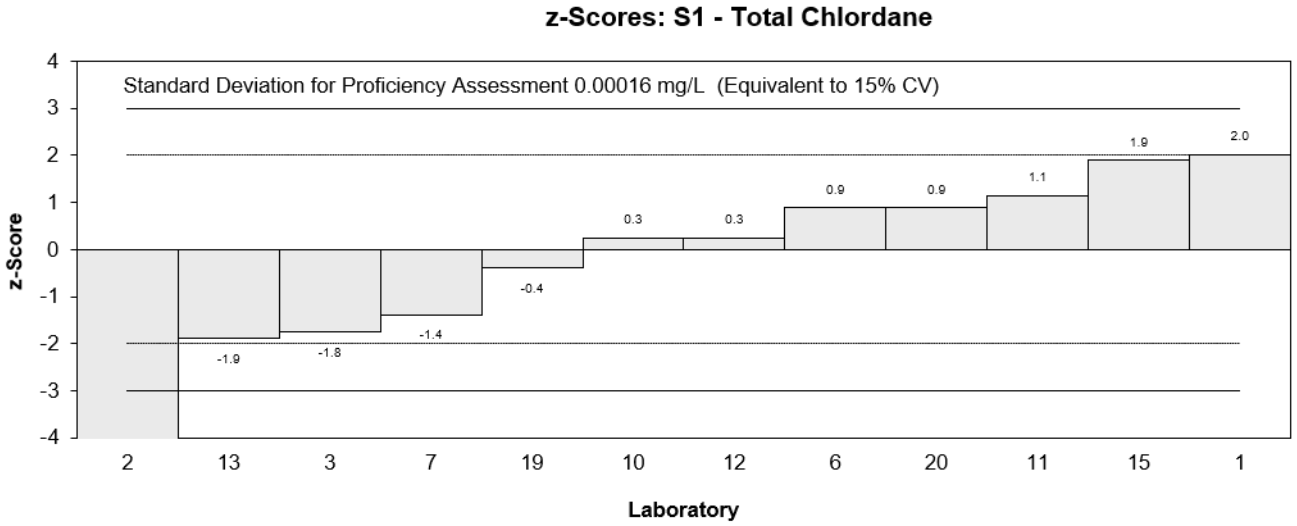
Lab. Code	Result	Uncertainty	Rec	z	E_n
1*	0.0021	0.0005	NR	2.00▼	
2*	0.00012	0.00004	NR	-5.91	-4.84
3	0.00078	0.00023	NR	-1.76	-0.94
4	NT	NT	NT		
5	NT	NT	NT		
6	0.0012	0.0005	NR	0.88	0.26
7	0.00084	0.00025	30	-1.38	-0.70
9	NT	NT	NT		
10	0.0011	0.00033	NR	0.25	0.11
11	0.00124	0.00055	NR	1.13	0.31
12	0.0011	0.0003	102	0.25	0.11
13	0.00076	0.00030	NR	-1.89	-0.84
14	<0.0005	NR	79.4		
15	0.00136	0.0004	NR	1.89	0.68
16	<0.0005	0.0005	NR		
17	<0.002	NR	NR		
18	NT	NT	NT		
19	0.001	0.0003	NR	-0.38	-0.17
20	0.0012	0.0005	NR	0.88	0.26
21	NT	NT	NT		

* Outlier, see Section 4.2; ▼ Adjusted Score, see Section 6.3

Statistics

Assigned Value	0.00106	0.00019
Spike Value	0.00197	0.00010
Robust Average	0.00106	0.00022
Max Acceptable Result	0.00256	
Median	0.00110	0.00021
Mean	0.00107	
N	12	
Max	0.0021	
Min	0.00012	
Robust SD	0.00031	
Robust CV	29%	


Kernel Density
Density
Result
Results: S1 - Total Chlordane
Assigned Value = 0.00106 ± 0.00019 mg/L
Maximum Acceptable Result = 0.00256 mg/L
Results (mg/L)
Laboratory
2 13 3 7 19 10 12 6 20 11 15 1 4 5 9 14 16 17 18 21 Md RA SV


z-Scores: S1 - Total Chlordane
Standard Deviation for Proficiency Assessment 0.00016 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
2 13 3 7 19 10 12 6 20 11 15 1
-1.9 -1.8 -1.4 -0.4 0.3 0.3 0.9 0.9 1.1 1.9 2.0

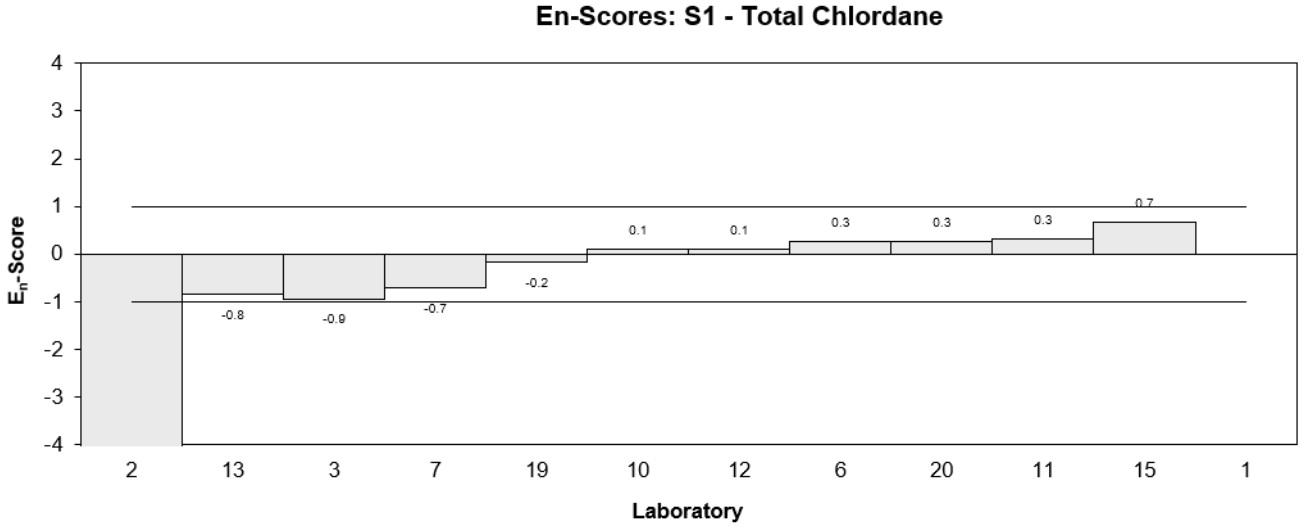

En-Scores: S1 - Total Chlordane
En-Score
Laboratory
2 13 3 7 19 10 12 6 20 11 15 1
-0.8 -0.9 -0.7 -0.2 0.1 0.1 0.3 0.3 0.3 0.7

Figure 4

Table 10

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	Total Cypermethrin
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	0.635	0.2	NR
2	NT	NT	NT
3	NT	NT	NT
4	NT	NT	NT
5	NT	NT	NT
6	0.56	0.17	NR
7	NT	NT	NT
9	NT	NT	NT
10	< 0.00005	NR	NR
11	0.34	0.15	NR
12	0.378	0.083	92
13	NT	NT	NT
14	0.137	0.048	79.6
15	< 0.2	NR	NR
16	0.0889	0.0885	NR
17	NT	NT	NT
18	NT	NT	NT
19	NT	NT	NT
20	0.14	0.058	NR
21	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	0.401	0.020
Robust Average	0.33	0.23
Median	0.34	0.28
Mean	0.33	
N	7	
Max	0.635	
Min	0.0889	
Robust SD	0.24	
Robust CV	75%	

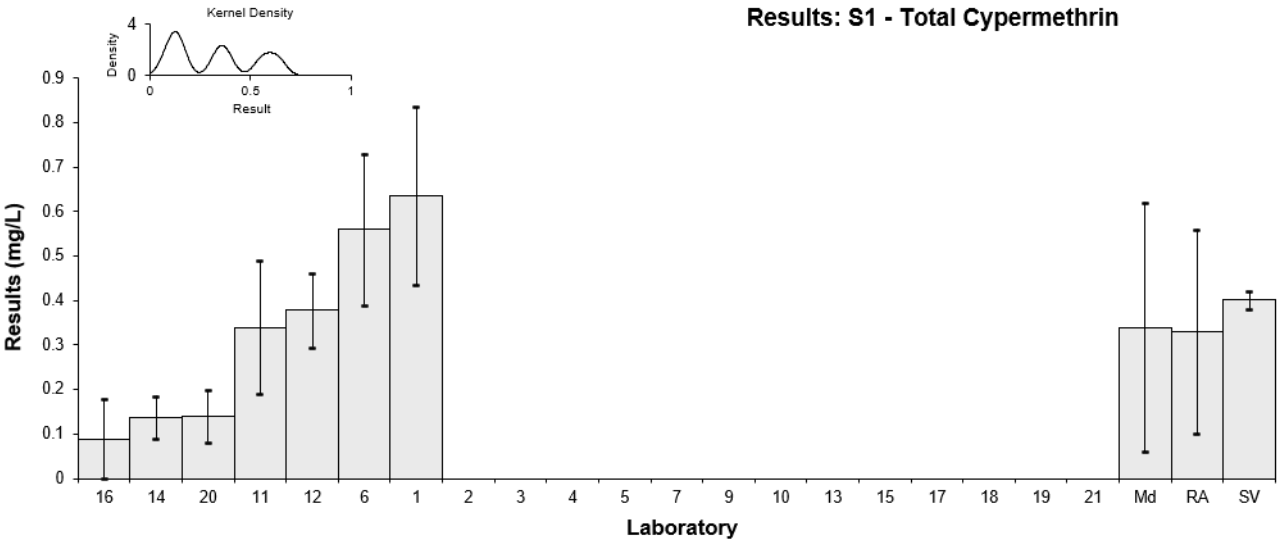

Results: S1 - Total Cypermethrin
Kernel Density
Density
Result
Results (mg/L)
Laboratory
16
14
20
11
12
6
1
2
3
4
5
7
9
10
13
15
17
18
19
21
Md
RA
SV

Figure 5

Table 11

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	p,p'-DDT
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	0.00866	0.003	NR
2	0.00074	0.00022	NR
3	0.00054	0.00016	NR
4	NT	NT	NT
5	NT	NT	NT
6	0.0056	0.002	NR
7	0.0058	0.0017	30
9	0.007	0.003	NR
10	0.0008	0.00024	NR
11	0.0044	0.002	NR
12	0.0042	0.0014	92
13	0.00390	0.00117	NR
14	<0.0020	NR	79.4
15	0.0087	0.003	NR
16	<0.0020	0.002	NR
17	<0.01	NR	NR
18	0.0036	0.00108	NR
19	0.008	0.0024	NR
20	0.0046	0.0018	NR
21	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	0.00824	0.00041
Robust Average	0.0048	0.0021
Median	0.0045	0.0019
Mean	0.0048	
N	14	
Max	0.0087	
Min	0.00054	
Robust SD	0.0031	
Robust CV	66%	

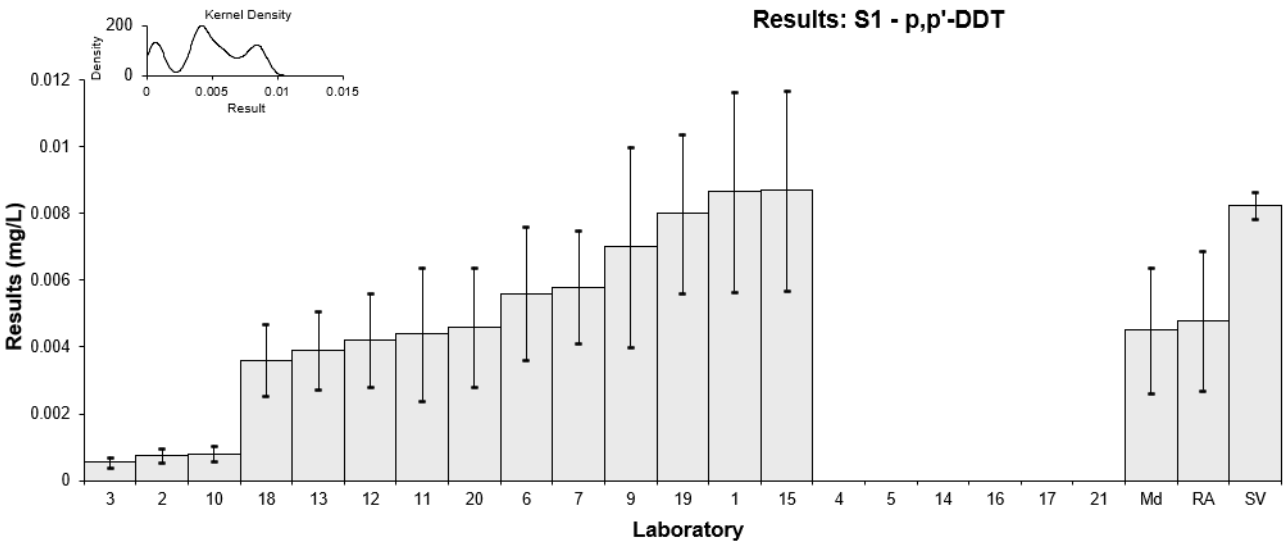

Results: S1 - p,p'-DDT
Kernel Density
Density
200
0
0
0.005
0.01
0.015
Result
Results (mg/L)
0.012
0.01
0.008
0.006
0.004
0.002
0
3
2
10
18
13
12
11
20
6
7
9
19
1
15
4
5
14
16
17
21
Md
RA
SV
Laboratory

Figure 6

Table 12

Sample Details

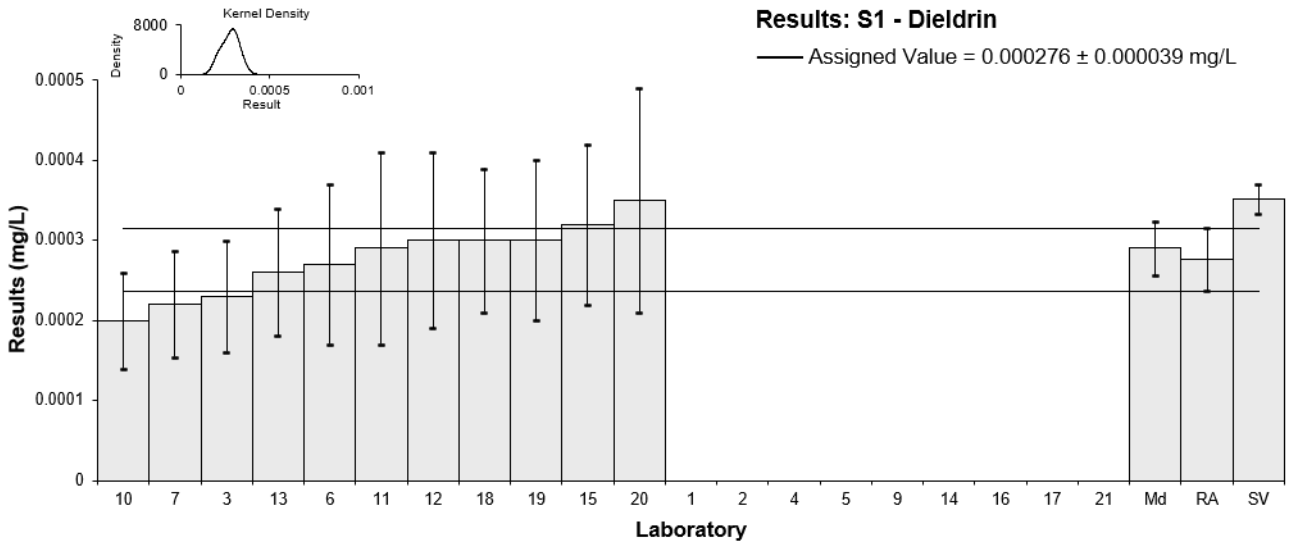
Sample No.	S1
Matrix	Potable Water
Analyte	Dieldrin
Unit	mg/L

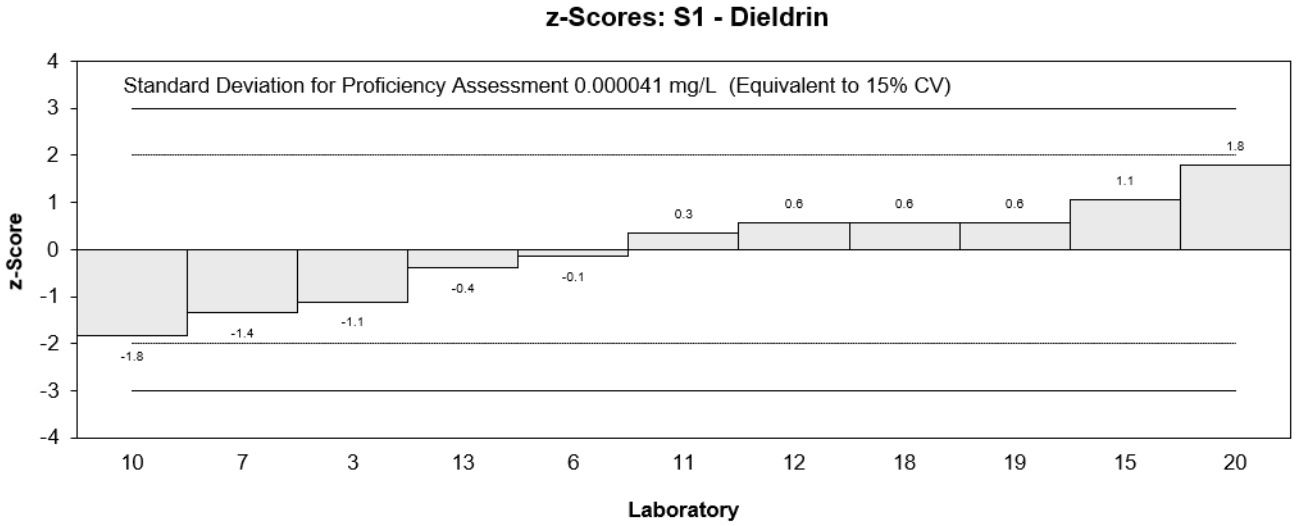
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	<0.0005	NR	NR		
2	<0.00005	NR	NR		
3	0.00023	0.000069	NR	-1.11	-0.58
4	NT	NT	NT		
5	NT	NT	NT		
6	0.00027	0.0001	NR	-0.14	-0.06
7	0.00022	0.000066	30	-1.35	-0.73
9	<0.001	0.001	NR		
10	0.00020	0.00006	NR	-1.84	-1.06
11	0.00029	0.00012	NR	0.34	0.11
12	0.0003	0.00011	94	0.58	0.21
13	0.00026	0.000079	NR	-0.39	-0.18
14	<0.0005	NR	79.4		
15	0.00032	0.0001	NR	1.06	0.41
16	<0.0005	0.0004	NR		
17	<0.001	NR	NR		
18	0.0003	0.00009	NR	0.58	0.24
19	0.0003	0.0001	NR	0.58	0.22
20	0.00035	0.00014	NR	1.79	0.51
21	NT	NT	NT		

Statistics

Assigned Value	0.000276	0.000039
Spike Value	0.000352	0.000018
Robust Average	0.000276	0.000039
Median	0.000290	0.000034
Mean	0.000276	
N	11	
Max	0.00035	
Min	0.00020	
Robust SD	0.000052	
Robust CV	19%	


Kernel Density
Density
8000
0
0
0.0005
0.001
Result
Results: S1 - Dieldrin
Assigned Value = 0.000276 ± 0.000039 mg/L
Results (mg/L)
0.0005
0.0004
0.0003
0.0002
0.0001
0
10 7 3 13 6 11 12 18 19 15 20 1 2 4 5 9 14 16 17 21 Md RA SV
Laboratory


z-Scores: S1 - Dieldrin
Standard Deviation for Proficiency Assessment 0.000041 mg/L (Equivalent to 15% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.8
-1.4
-1.1
-0.4
-0.1
0.3
0.6
0.6
0.6
1.1
1.8
10 7 3 13 6 11 12 18 19 15 20
Laboratory

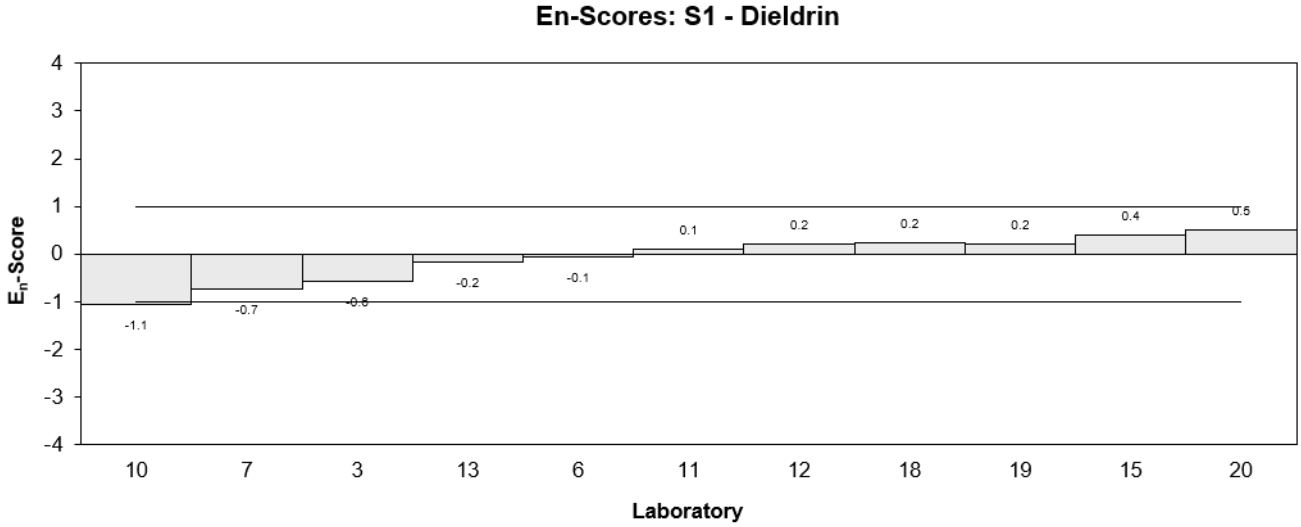

En-Scores: S1 - Dieldrin
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.1
-0.7
-0.6
-0.2
-0.1
0.1
0.2
0.2
0.2
0.4
0.6
10 7 3 13 6 11 12 18 19 15 20
Laboratory

Figure 7

Table 13

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	Total Endosulfan
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	<0.005	NR	NR
2	<0.00001	NR	NR
3	<0.0004	NR	NR
4	NT	NT	NT
5	NT	NT	NT
6	0.00029	0.0001	NR
7	0.00023	0.000069	30
9	NT	NT	NT
10	0.0002	0.00006	NR
11	0.00027	0.00013	NR
12	0.0049	0.0014	100
13	0.00869	0.00261	NR
14	0.0016	0.0004	79.4
15	0.00022	0.0001	NR
16	0.0031	0.0024	NR
17	<0.002	NR	NR
18	0.0002	0.00006	NR
19	0.0035	0.0011	NR
20	<0.0001	NR	NR
21	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	0.0300	0.0015
Robust Average	0.0018	0.0017
Median	0.00029	0.00010
Mean	0.0021	
N	11	
Max	0.00869	
Min	0.0002	
Robust SD	0.0023	
Robust CV	130%	

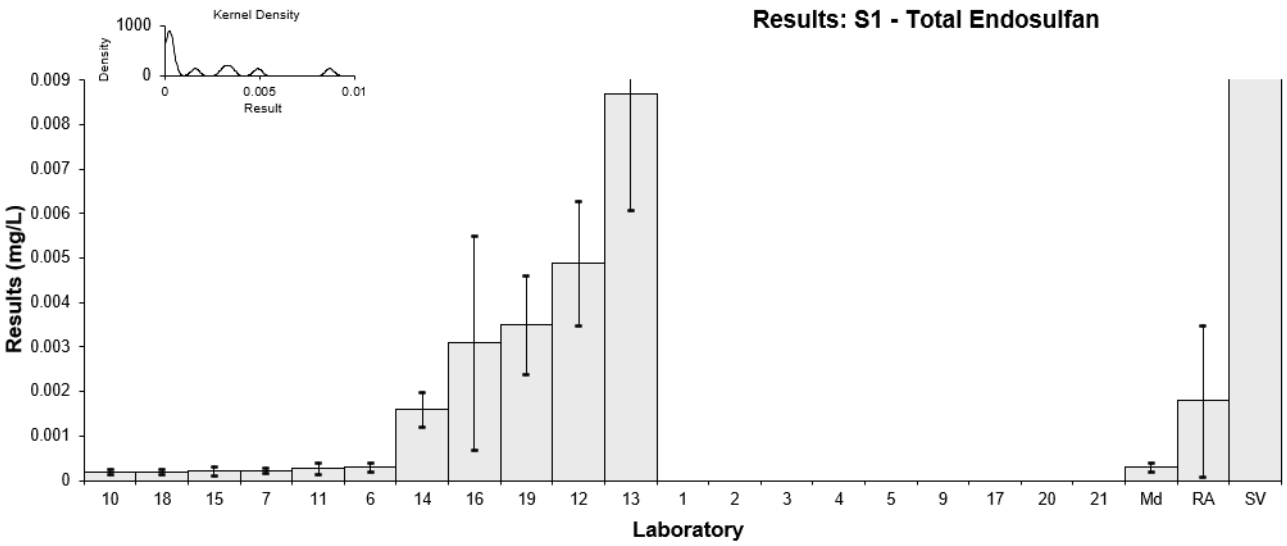

Results: S1 - Total Endosulfan
Kernel Density
Density
1000
0
0
0.005
0.01
Result
Results (mg/L)
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
10
18
15
7
11
6
14
16
19
12
13
1
2
3
4
5
9
17
20
21
Md
RA
SV
Laboratory

Figure 8

Table 14

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	Maldison
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	Rec
1**	0.0000588	0.00002	NR
2	0.045	0.014	NR
3	0.021	0.0063	NR
4	NT	NT	NT
5	<0.0005	NR	NR
6**	0.00011	0.00005	NR
7	< 0.002	NR	NR
9	<0.001	0.001	NR
10	0.0710	0.021	NR
11	<0.00017	0.000051	NR
12	0.039	0.011	97
13	0.0452	0.0054	NR
14	0.0039	0.0012	85.2
15	< 0.002	NR	NR
16	0.0176	0.0144	NR
17	<0.001	NR	NR
18	NT	NT	NT
19	0.02	0.006	NR
20**	0.00022	0.0001	NR
21	NT	NT	NT

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	Not Set	
Spike Value	0.151	0.008
Robust Average	0.032	0.020
Median	0.030	0.018
Mean	0.033	
N	8	
Max	0.0710	
Min	0.0039	
Robust SD	0.023	
Robust CV	71%	

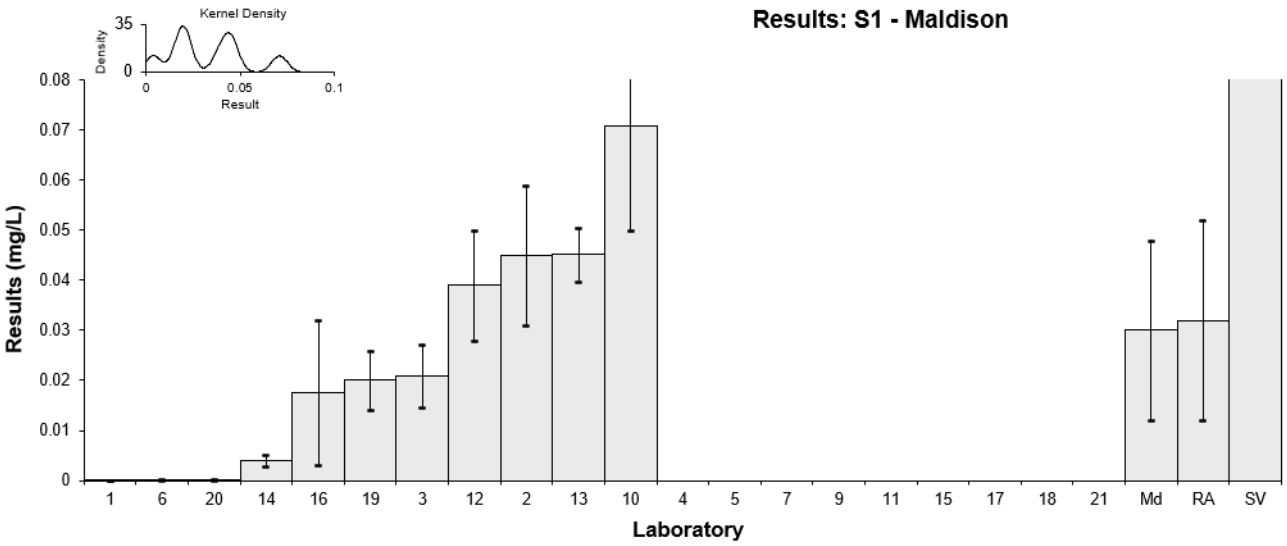

Results: S1 - Maldison
Kernel Density
Density
35
0
0
0.05
0.1
Result
Results (mg/L)
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
1
6
20
14
16
19
3
12
2
13
10
4
5
7
9
11
15
17
18
21
Md
RA
SV
Laboratory

Figure 9

Table 15

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	Picloram
Unit	mg/L

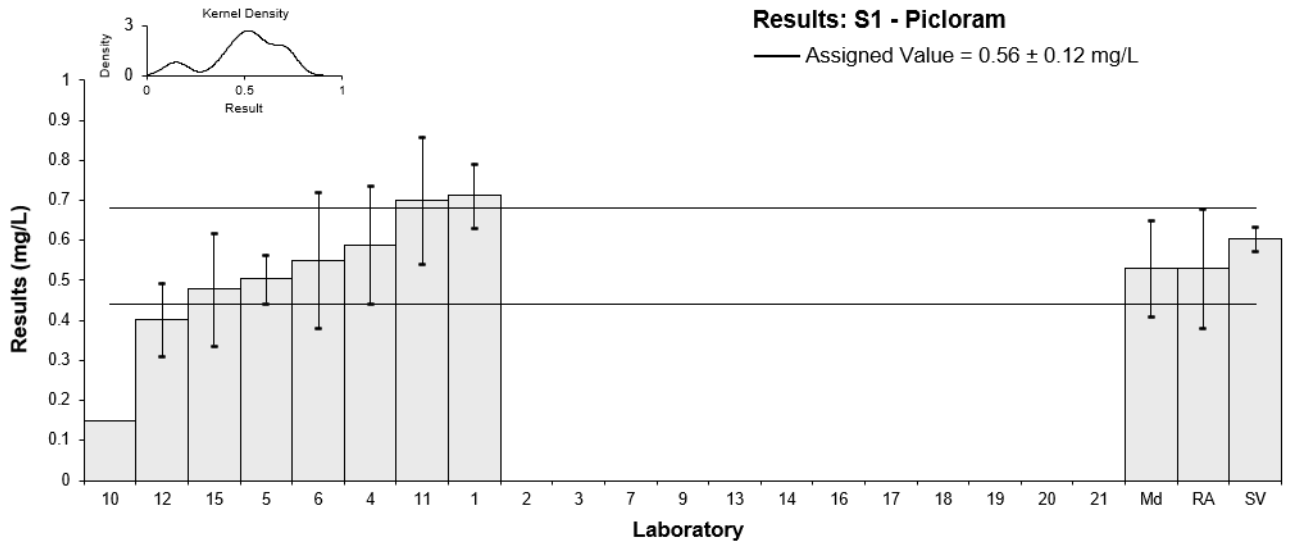
Participant Results

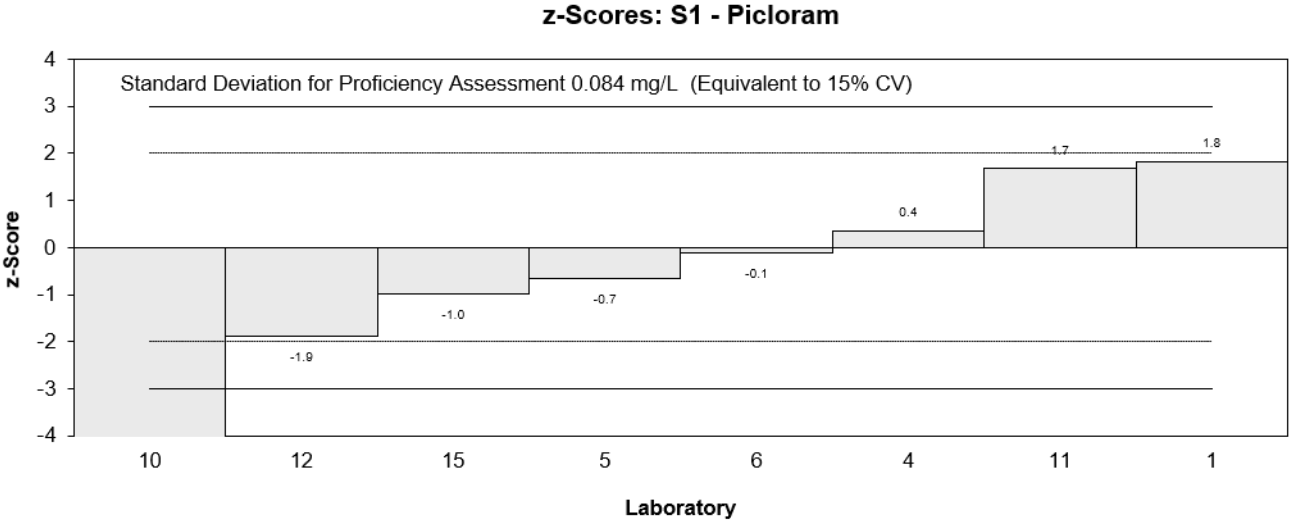
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.712	0.08	NR	1.81	1.05
2	NT	NT	NT		
3	NT	NT	NT		
4	0.589	0.147	100	0.35	0.15
5	0.504	0.06103	92.00	-0.67	-0.42
6	0.55	0.17	NR	-0.12	-0.05
7	NT	NT	NT		
9	NT	NT	NT		
10*	0.15	NR	NR	-4.88	-3.42
11	0.7	0.16	NR	1.67	0.70
12	0.402	0.092	96	-1.88	-1.04
13	NT	NT	NT		
14	NT	NT	NT		
15	0.4777	0.14	NR	-0.98	-0.45
16	NT	NT	NT		
17	NT	NT	NT		
18	NT	NT	NT		
19	NT	NT	NT		
20	NT	NT	NT		
21	NT	NT	NT		

* Outlier, see Section 4.2

Statistics

Assigned Value	0.56	0.12
Spike Value	0.604	0.030
Robust Average	0.53	0.15
Median	0.53	0.12
Mean	0.51	
N	8	
Max	0.712	
Min	0.15	
Robust SD	0.16	
Robust CV	31%	


Kernel Density
Density
Result
Results: S1 - Picloram
Assigned Value = 0.56 ± 0.12 mg/L
Results (mg/L)
Laboratory
10 12 15 5 6 4 11 1 2 3 7 9 13 14 16 17 18 19 20 21 Md RA SV


z-Scores: S1 - Picloram
Standard Deviation for Proficiency Assessment 0.084 mg/L (Equivalent to 15% CV)
z-Score
-1.9
-1.0
-0.7
-0.1
0.4
1.7
1.8
Laboratory
10 12 15 5 6 4 11 1

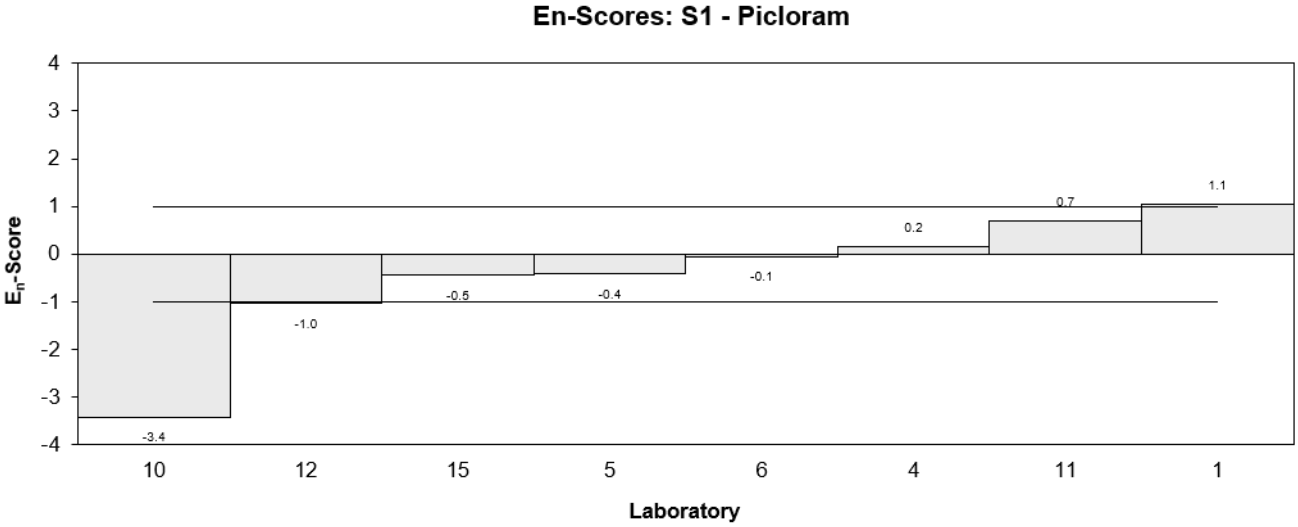

En-Scores: S1 - Picloram
En-Score
-3.4
-1.0
-0.5
-0.4
-0.1
0.2
0.7
1.1
Laboratory
10 12 15 5 6 4 11 1

Figure 10

Table 16

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	Pirimiphos-methyl
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	0.0405	0.01	NR
2	<0.00005	NR	NR
3	0.063	0.019	NR
4	NT	NT	NT
5	0.0582	0.00292	99.43
6	NT	NT	NT
7	0.07	0.021	30
9	NT	NT	NT
10	0.059	0.0177	NR
11	0.085	0.038	NR
12	0.105	0.026	91
13	NT	NT	NT
14	NT	NT	NT
15	0.064	0.019	NR
16	NT	NT	NT
17	0.074	0.022	NR
18	NT	NT	NT
19	NT	NT	NT
20	0.067	0.027	NR
21	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	0.152	0.008
Robust Average	0.068	0.012
Median	0.0655	0.0081
Mean	0.069	
N	10	
Max	0.105	
Min	0.0405	
Robust SD	0.015	
Robust CV	22%	

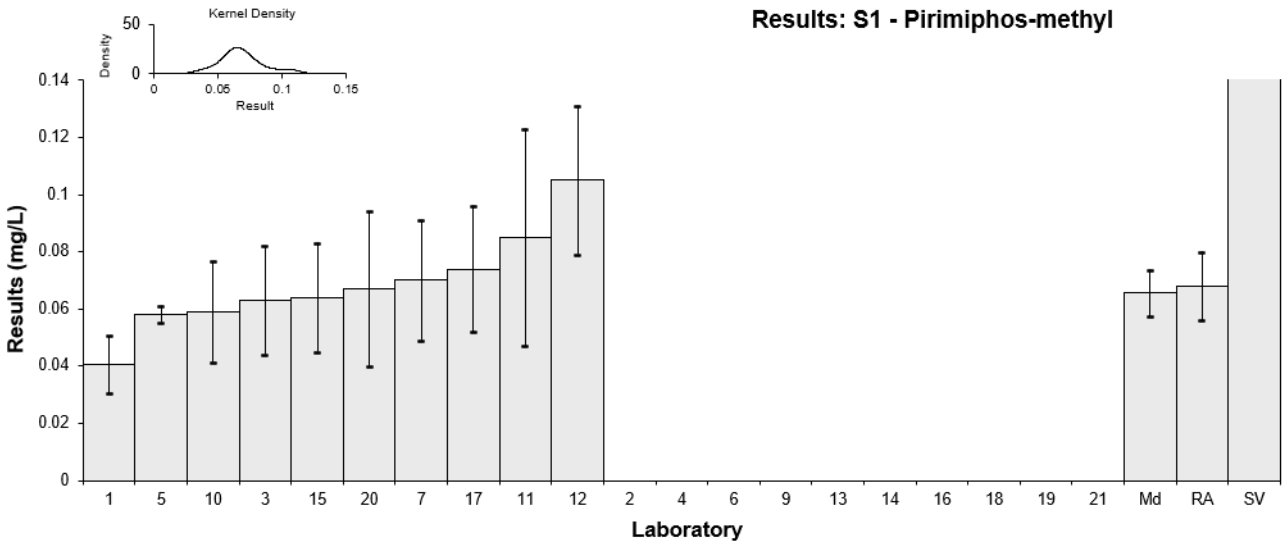

Results: S1 - Pirimiphos-methyl
Kernel Density
Density
50
0
0
0.05
0.1
0.15
Result
Results (mg/L)
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
1
5
10
3
15
20
7
17
11
12
2
4
6
9
13
14
16
18
19
21
Md
RA
SV
Laboratory

Figure 11

Table 17

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	Total Propiconazole
Unit	mg/L

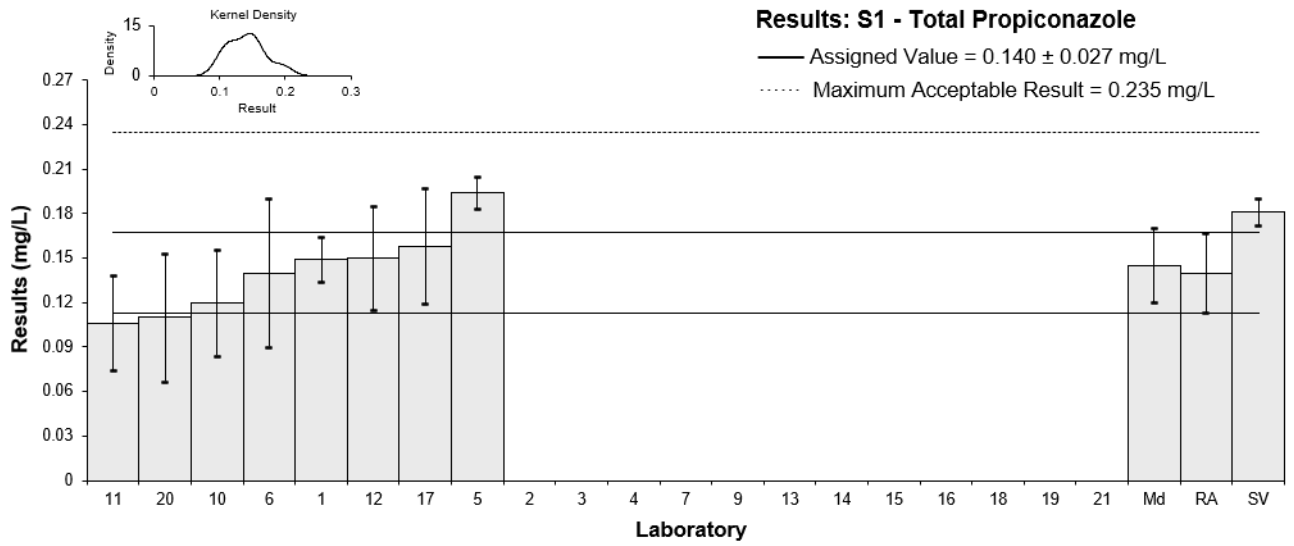
Participant Results

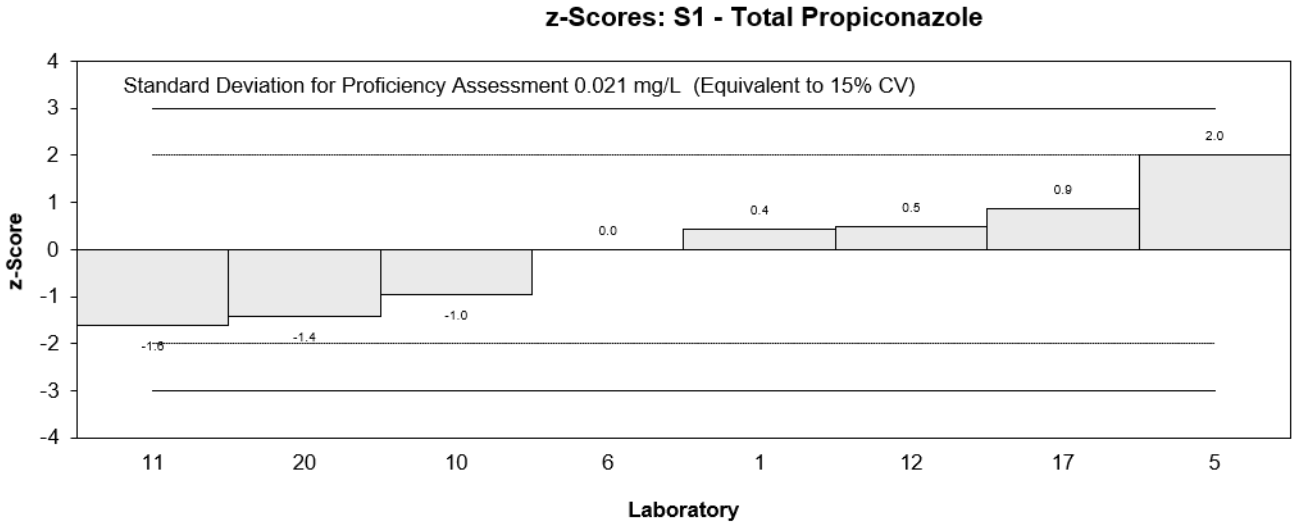
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.149	0.015	NR	0.43	0.29
2	NT	NT	NT		
3	NT	NT	NT		
4	NT	NT	NT		
5	0.194	0.01069	97.03	2.00▼	
6	0.14	0.05	NR	0.00	0.00
7	NT	NT	NT		
9	NT	NT	NT		
10	0.12	0.0360	NR	-0.95	-0.44
11	0.106	0.032	NR	-1.62	-0.81
12	0.15	0.035	98	0.48	0.23
13	NT	NT	NT		
14	NT	NT	NT		
15	NT	NT	NT		
16	NT	NT	NT		
17	0.158	0.039	NR	0.86	0.38
18	NT	NT	NT		
19	NT	NT	NT		
20	0.11	0.043	NR	-1.43	-0.59
21	NT	NT	NT		

▼ Adjusted Score, see Section 6.3

Statistics

Assigned Value	0.140	0.027
Spike Value	0.181	0.009
Robust Average	0.140	0.027
Max Acceptable Result	0.235	
Median	0.145	0.025
Mean	0.141	
N	8	
Max	0.194	
Min	0.106	
Robust SD	0.03	
Robust CV	22%	


Kernel Density
Density
Result
Results: S1 - Total Propiconazole
Assigned Value = 0.140 ± 0.027 mg/L
Maximum Acceptable Result = 0.235 mg/L
Results (mg/L)
Laboratory
11 20 10 6 1 12 17 5 2 3 4 7 9 13 14 15 16 18 19 21 Md RA SV


z-Scores: S1 - Total Propiconazole
Standard Deviation for Proficiency Assessment 0.021 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
11 20 10 6 1 12 17 5
-1.6
-1.4
-1.0
0.0
0.4
0.5
0.9
2.0

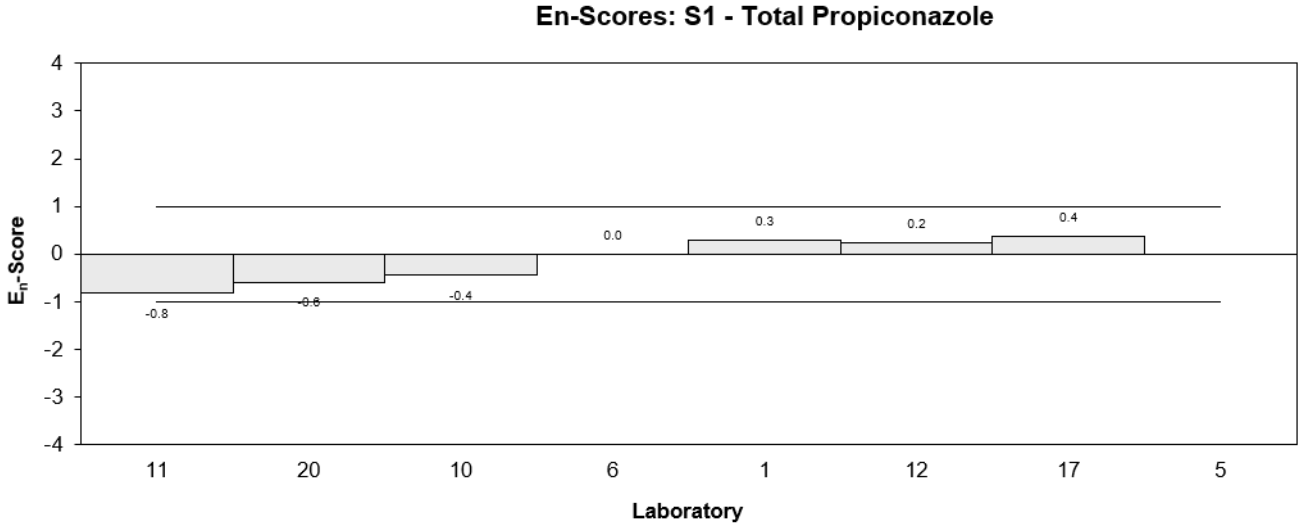

En-Scores: S1 - Total Propiconazole
En-Score
Laboratory
11 20 10 6 1 12 17 5
-0.8
-0.6
-0.4
0.0
0.3
0.2
0.4

Figure 12

Table 18

Sample Details

Sample No.	S2
Matrix	Potable Water
Analyte	Acephate
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	NT	NT	NT
2	NT	NT	NT
3	NT	NT	NT
4	NT	NT	NT
5	NT	NT	NT
6	0.0083	0.003	NR
7	NT	NT	NT
9	NS	NS	NS
10	NT	NT	NT
11	NT	NT	NT
12	NT	NT	NT
13	NT	NT	NT
14	NT	NT	NT
15	NT	NT	NT
16	NT	NT	NT
17	0.005	0.001	NR
18	NT	NT	NT
19	NT	NT	NT
20	0.0077	0.0038	NR
21	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	0.00991	0.00050
Robust Average	NA (N<6)	
Median	0.0077	0.0013
Mean	0.0070	
N	3	
Max	0.0083	
Min	0.005	
Robust SD	NA (N<6)	
Robust CV	NA (N<6)	

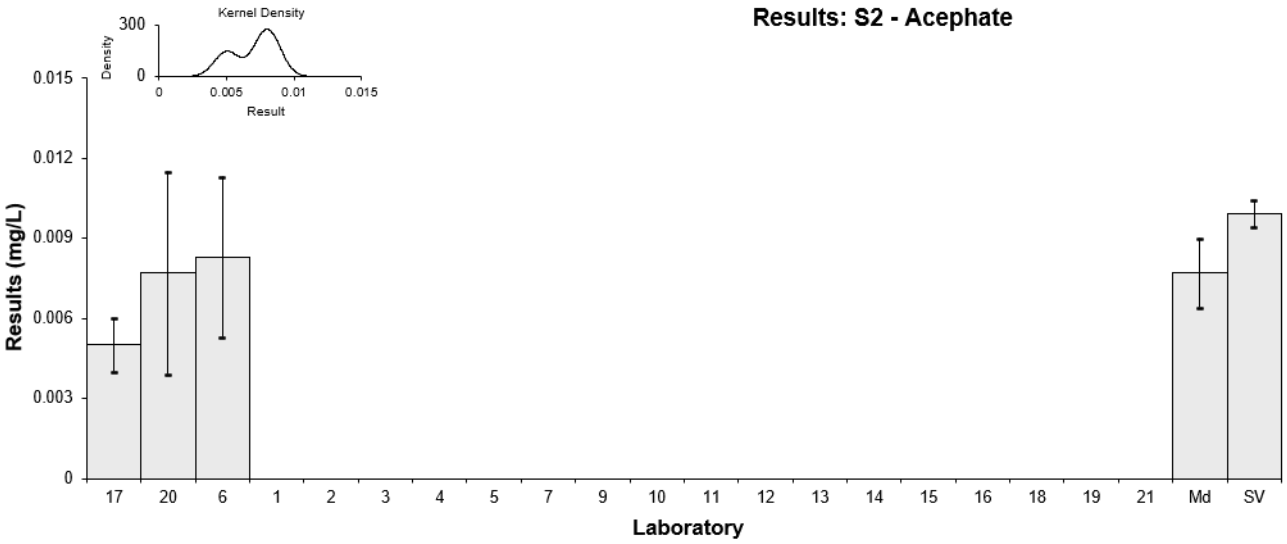

Results: S2 - Acephate
Kernel Density
Density
300
0
0
0.005
0.01
0.015
Result
Results (mg/L)
0.015
0.012
0.009
0.006
0.003
0
17
20
6
1
2
3
4
5
7
9
10
11
12
13
14
15
16
18
19
21
Md
SV
Laboratory

Figure 13

Table 19

Sample Details

Sample No.	S2
Matrix	Potable Water
Analyte	Atrazine
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	0.0263	0.003	NR
2	0.015	0.005	NR
3	NT	NT	NT
4	0.025	0.00625	108
5	0.0296	0.00159	102.05
6	0.019	0.009	NR
7	NT	NT	NT
9	NS	NS	NS
10	0.020	0.0060	NR
11	0.0112	0.0054	NR
12	0.024	0.006	96
13	NT	NT	NT
14	0.0178	0.0046	88.2
15	0.025	0.007	NR
16	0.0116	0.0081	NR
17	0.038	0.001	NR
18	NT	NT	NT
19	NT	NT	NT
20	0.020	0.008	NR
21	0.0321	0.0096	NR

Statistics

Assigned Value	Not Set	
Spike Value	0.0251	0.0013
Robust Average	0.0222	0.0054
Median	0.0220	0.0042
Mean	0.0225	
N	14	
Max	0.038	
Min	0.0112	
Robust SD	0.0081	
Robust CV	36%	

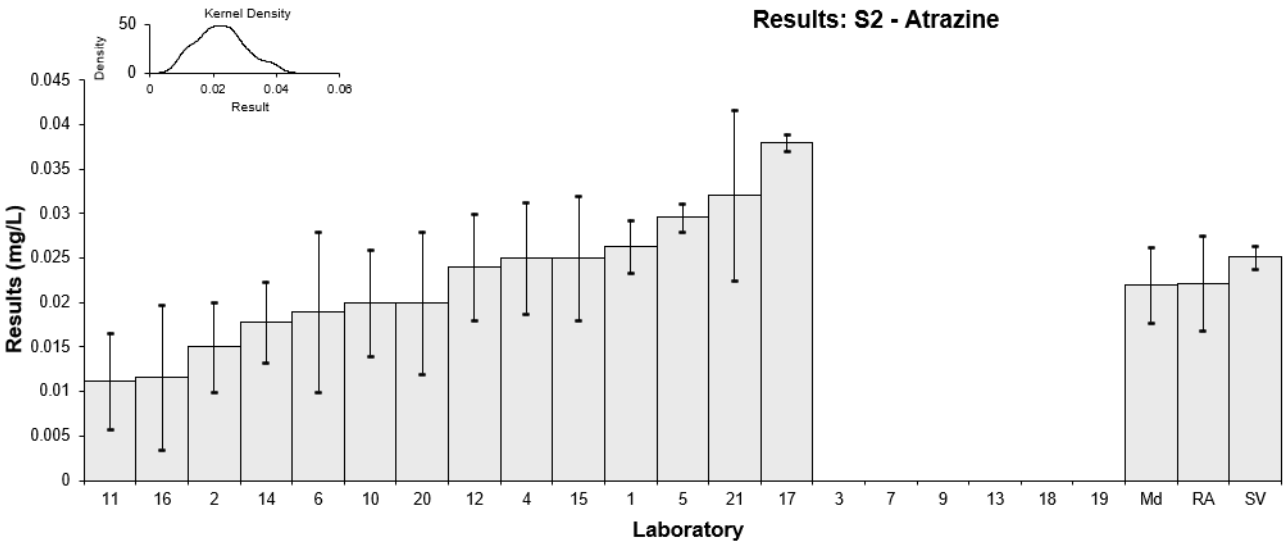

Results: S2 - Atrazine
Kernel Density
Density
50
0
0
0.02
0.04
0.06
Result
Results (mg/L)
0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
11
16
2
14
6
10
20
12
4
15
1
5
21
17
3
7
9
13
18
19
Md
RA
SV
Laboratory

Figure 14

Table 20

Sample Details

Sample No.	S2
Matrix	Potable Water
Analyte	Bromacil
Unit	mg/L

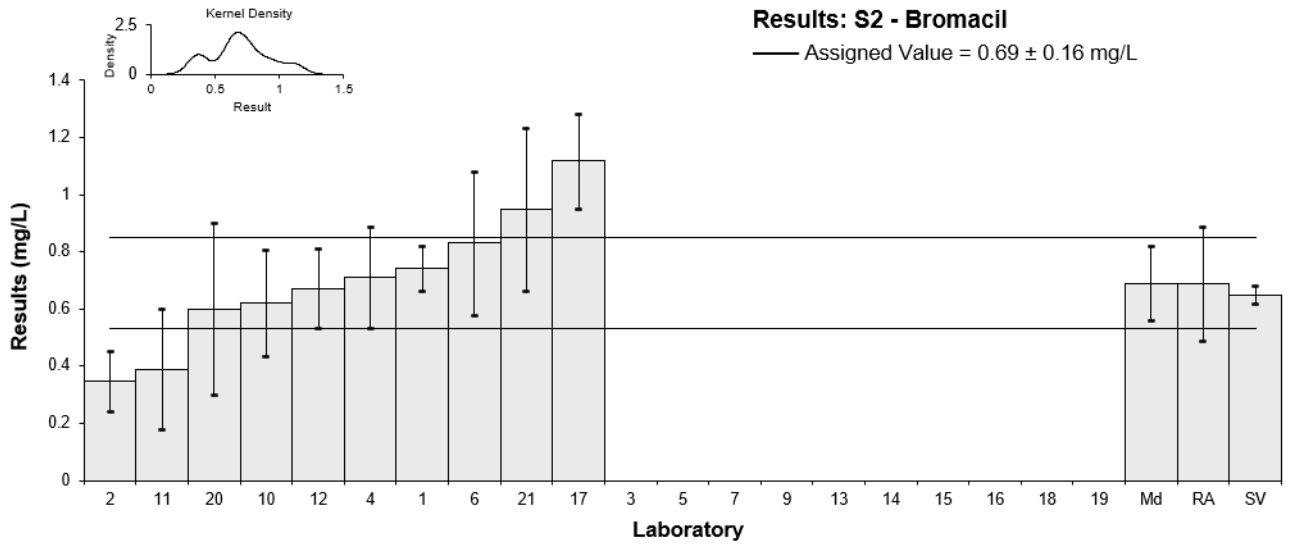
Participant Results

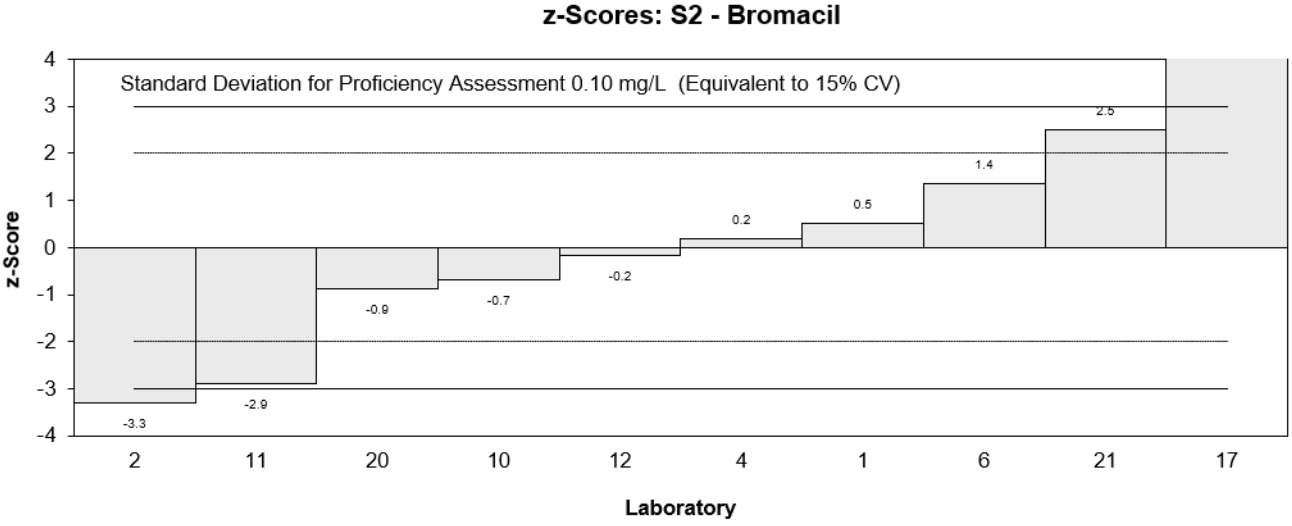
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.743	0.08	NR	0.51	0.30
2*	0.3469	0.104	NR	-3.31	-1.80
3	NT	NT	NT		
4	0.710	0.178	106	0.19	0.08
5	NT	NT	NT		
6	0.83	0.25	NR	1.35	0.47
7	NT	NT	NT		
9	NS	NS	NS		
10	0.62	0.18600	NR	-0.68	-0.29
11	0.39	0.21	NR	-2.90	-1.14
12	0.672	0.14	91	-0.17	-0.08
13	NT	NT	NT		
14	NT	NT	NT		
15	NT	NT	NT		
16	NT	NT	NT		
17*	1.117	0.168	NR	4.13	1.84
18	NT	NT	NT		
19	NT	NT	NT		
20	0.60	0.3	NR	-0.87	-0.26
21	0.9491	0.285	NR	2.50	0.79

* Outlier, see Section 4.2

Statistics

Assigned Value	0.69	0.16
Spike Value	0.650	0.033
Robust Average	0.69	0.20
Median	0.69	0.13
Mean	0.70	
N	10	
Max	1.117	
Min	0.3469	
Robust SD	0.26	
Robust CV	37%	


Kernel Density
Density
Result
Results: S2 - Bromacil
Assigned Value = 0.69 ± 0.16 mg/L
Results (mg/L)
Laboratory
2 11 20 10 12 4 1 6 21 17 3 5 7 9 13 14 15 16 18 19 Md RA SV


z-Scores: S2 - Bromacil
Standard Deviation for Proficiency Assessment 0.10 mg/L (Equivalent to 15% CV)
z-Score
-3.3
-2.9
-0.9
-0.7
-0.2
0.2
0.5
1.4
2.5
Laboratory
2 11 20 10 12 4 1 6 21 17

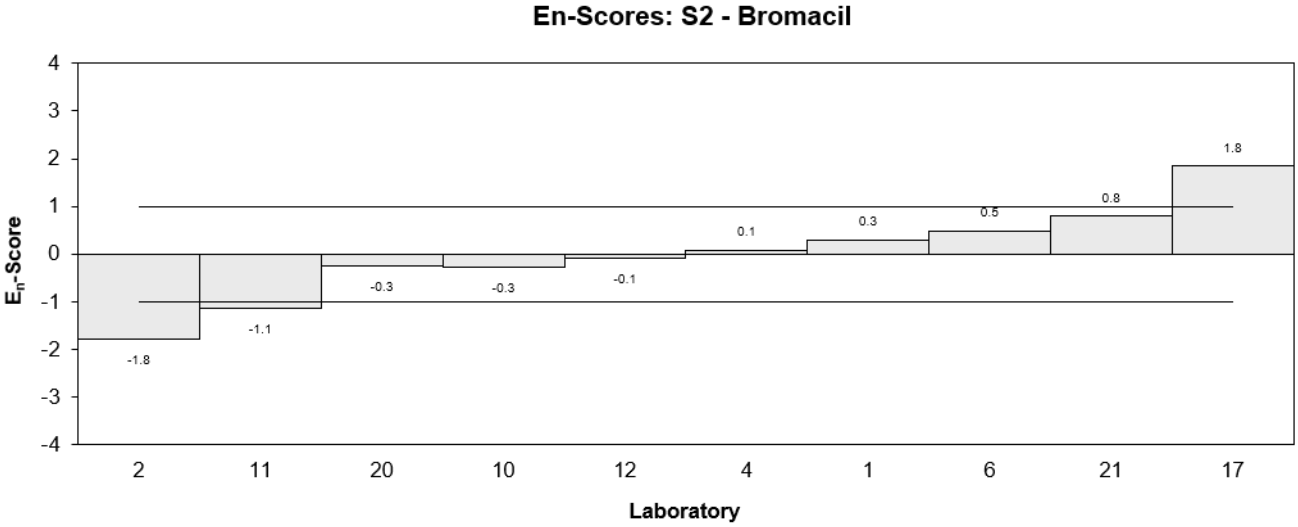

En-Scores: S2 - Bromacil
En-Score
-1.8
-1.1
-0.3
-0.3
-0.1
0.1
0.3
0.5
0.8
1.8
Laboratory
2 11 20 10 12 4 1 6 21 17

Figure 15

Table 21

Sample Details

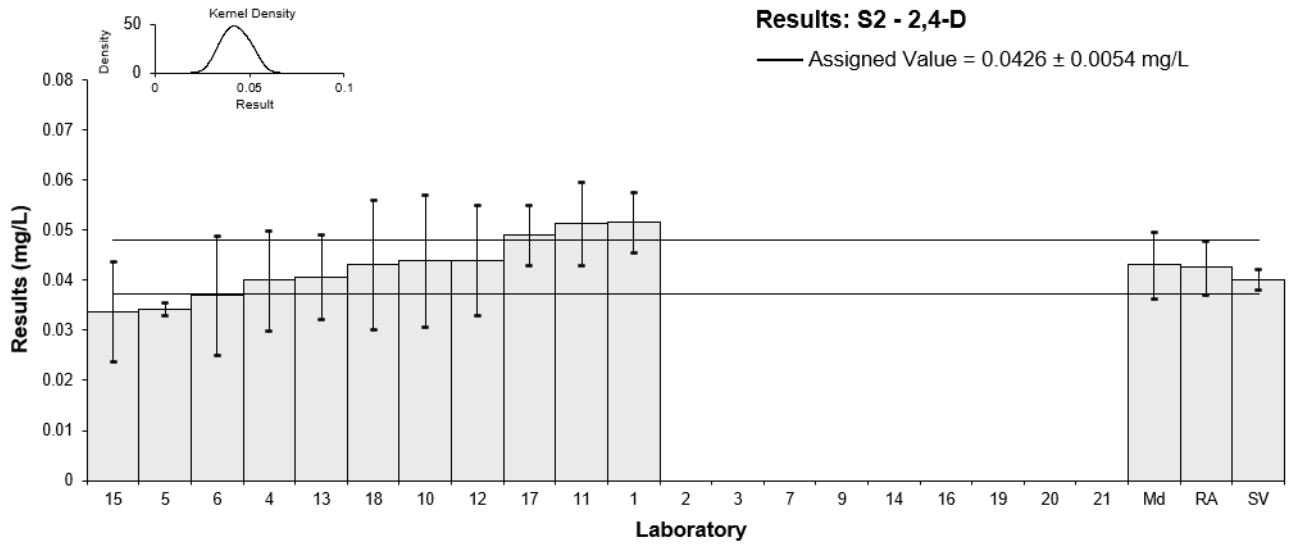
Sample No.	S2
Matrix	Potable Water
Analyte	2,4-D
Unit	mg/L

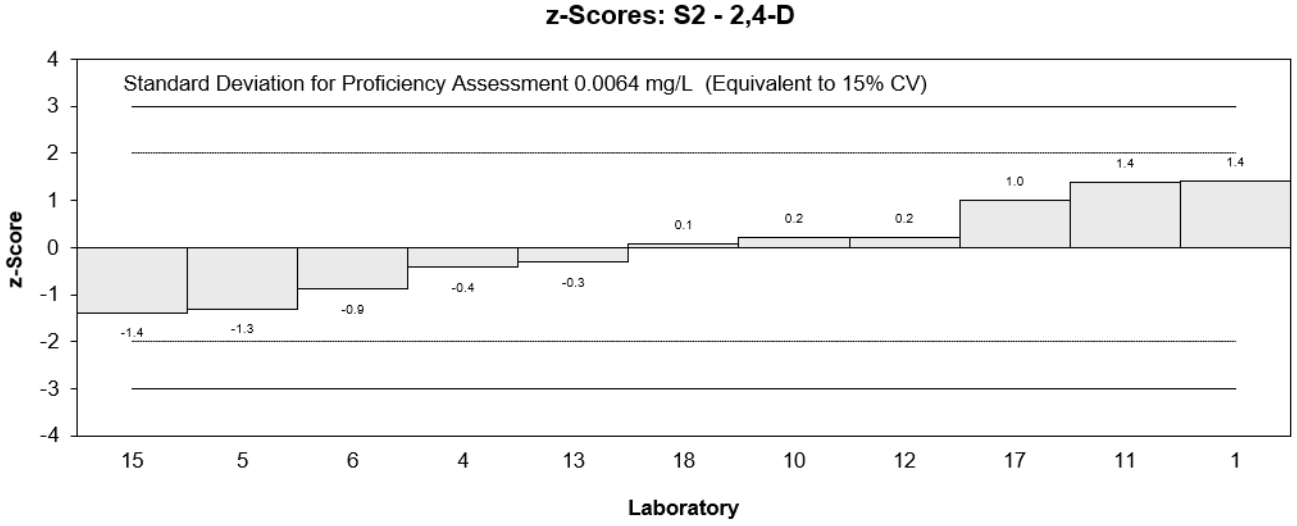
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.0517	0.006	NR	1.42	1.13
2	NT	NT	NT		
3	NT	NT	NT		
4	0.040	0.01	82	-0.41	-0.23
5	0.0343	0.00130	98.8	-1.30	-1.49
6	0.037	0.012	NR	-0.88	-0.43
7	NT	NT	NT		
9	NS	NS	NS		
10	0.044	0.0132	NR	0.22	0.10
11	0.0514	0.0083	NR	1.38	0.89
12	0.044	0.011	98	0.22	0.11
13	0.0407	0.0085	NR	-0.30	-0.19
14	NT	NT	NT		
15	0.0338	0.01	NR	-1.38	-0.77
16	NT	NT	NT		
17	0.049	0.006	NR	1.00	0.79
18	0.0431	0.01293	NR	0.08	0.04
19	NT	NT	NT		
20	NT	NT	NT		
21	NT	NT	NT		

Statistics

Assigned Value	0.0426	0.0054
Spike Value	0.0402	0.0020
Robust Average	0.0426	0.0054
Median	0.0431	0.0066
Mean	0.0426	
N	11	
Max	0.0517	
Min	0.0338	
Robust SD	0.0071	
Robust CV	17%	


Kernel Density
Density
Result
Results: S2 - 2,4-D
Assigned Value = 0.0426 ± 0.0054 mg/L
Results (mg/L)
Laboratory
15 5 6 4 13 18 10 12 17 11 1 2 3 7 9 14 16 19 20 21 Md RA SV


z-Scores: S2 - 2,4-D
Standard Deviation for Proficiency Assessment 0.0064 mg/L (Equivalent to 15% CV)
z-Score
-1.4 -1.3 -0.9 -0.4 -0.3 0.1 0.2 0.2 1.0 1.4 1.4
Laboratory
15 5 6 4 13 18 10 12 17 11 1

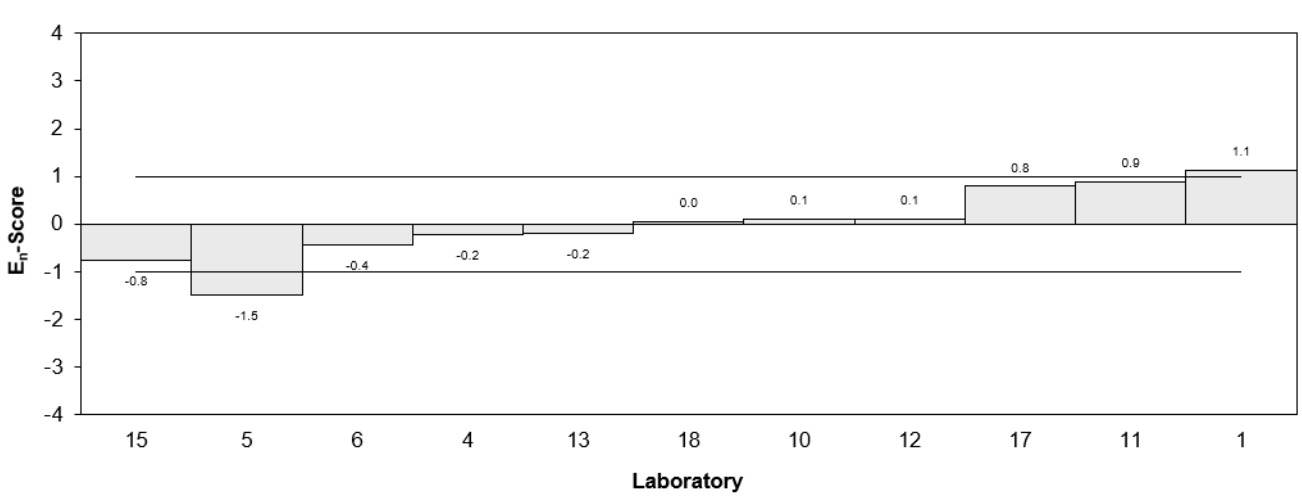

En-Scores: S2 - 2,4-D
En-Score
-0.8 -1.5 -0.4 -0.2 -0.2 0.0 0.1 0.1 0.8 0.9 1.1
Laboratory
15 5 6 4 13 18 10 12 17 11 1

Figure 16

Table 22

Sample Details

Sample No.	S2
Matrix	Potable Water
Analyte	Fipronil
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	NT	NT	NT
2	NT	NT	NT
3	NT	NT	NT
4	0.00118	0.000295	100
5	0.00145	0.00008	99.26
6	0.00083	0.0003	NR
7	NT	NT	NT
9	NS	NS	NS
10	0.0012	0.00036	NR
11	NT	NT	NT
12	NT	NT	NT
13	NT	NT	NT
14	0.0013	0.0003	82.5
15	NT	NT	NT
16	NT	NT	NT
17	0.002	0.001	NR
18	NT	NT	NT
19	NT	NT	NT
20	<0.002	NR	NR
21	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	0.00147	0.00007
Robust Average	0.00131	0.00042
Median	0.00125	0.00020
Mean	0.00133	
N	6	
Max	0.002	
Min	0.00083	
Robust SD	0.00041	
Robust CV	31%	

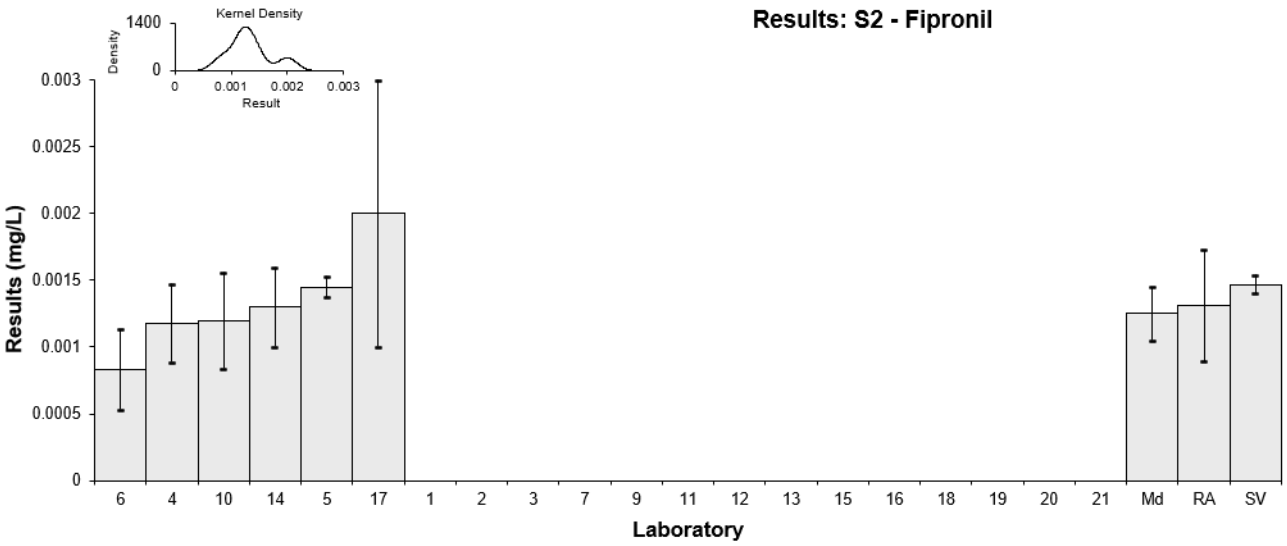

Results: S2 - Fipronil
Kernel Density
Density
1400
0
0
0.001
0.002
0.003
Result
Results (mg/L)
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
6
4
10
14
5
17
1
2
3
7
9
11
12
13
15
16
18
19
20
21
Md
RA
SV
Laboratory

Figure 17

Table 23

Sample Details

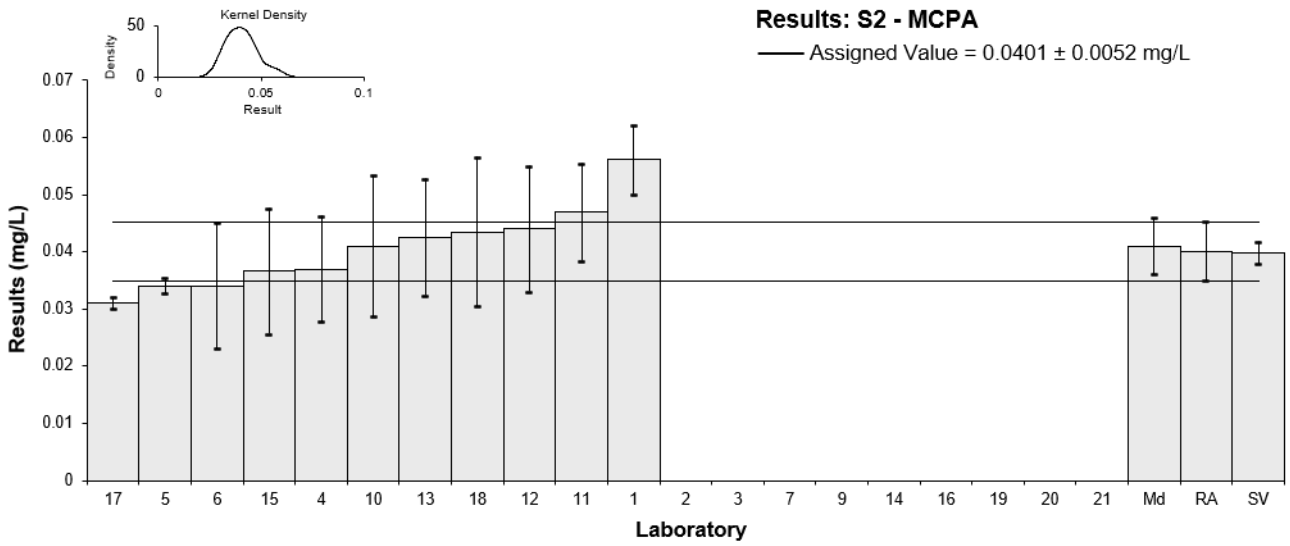
Sample No.	S2
Matrix	Potable Water
Analyte	MCPA
Unit	mg/L

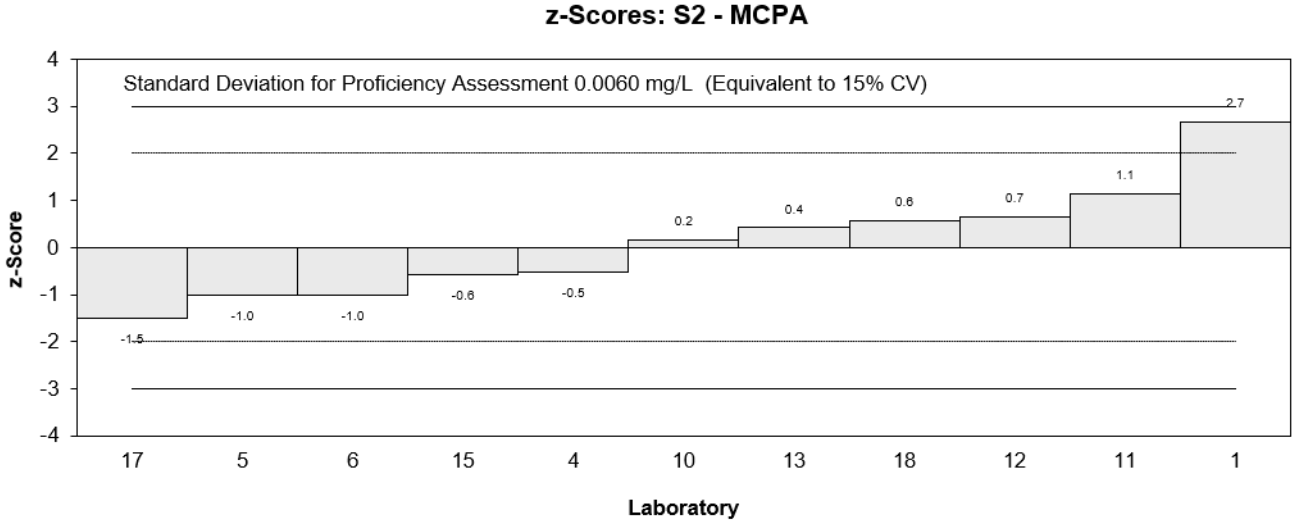
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.0561	0.006	NR	2.66	2.02
2	NT	NT	NT		
3	NT	NT	NT		
4	0.037	0.00925	88	-0.52	-0.29
5	0.0340	0.00133	101	-1.01	-1.14
6	0.034	0.011	NR	-1.01	-0.50
7	NT	NT	NT		
9	NS	NS	NS		
10	0.041	0.0123	NR	0.15	0.07
11	0.0469	0.0085	NR	1.13	0.68
12	0.044	0.011	110	0.65	0.32
13	0.0426	0.0102	NR	0.42	0.22
14	NT	NT	NT		
15	0.0366	0.011	NR	-0.58	-0.29
16	NT	NT	NT		
17	0.031	0.001	NR	-1.51	-1.72
18	0.0435	0.01305	NR	0.57	0.24
19	NT	NT	NT		
20	NT	NT	NT		
21	NT	NT	NT		

Statistics

Assigned Value	0.0401	0.0052
Spike Value	0.0398	0.0020
Robust Average	0.0401	0.0052
Median	0.0410	0.0049
Mean	0.0406	
N	11	
Max	0.0561	
Min	0.031	
Robust SD	0.0068	
Robust CV	17%	


Kernel Density
Density
Result
Results: S2 - MCPA
Assigned Value = 0.0401 ± 0.0052 mg/L
Results (mg/L)
Laboratory
17 5 6 15 4 10 13 18 12 11 1 2 3 7 9 14 16 19 20 21 Md RA SV


z-Scores: S2 - MCPA
Standard Deviation for Proficiency Assessment 0.0060 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
17 5 6 15 4 10 13 18 12 11 1
-1.5 -1.0 -1.0 -0.6 -0.5 0.2 0.4 0.6 0.7 1.1 2.7

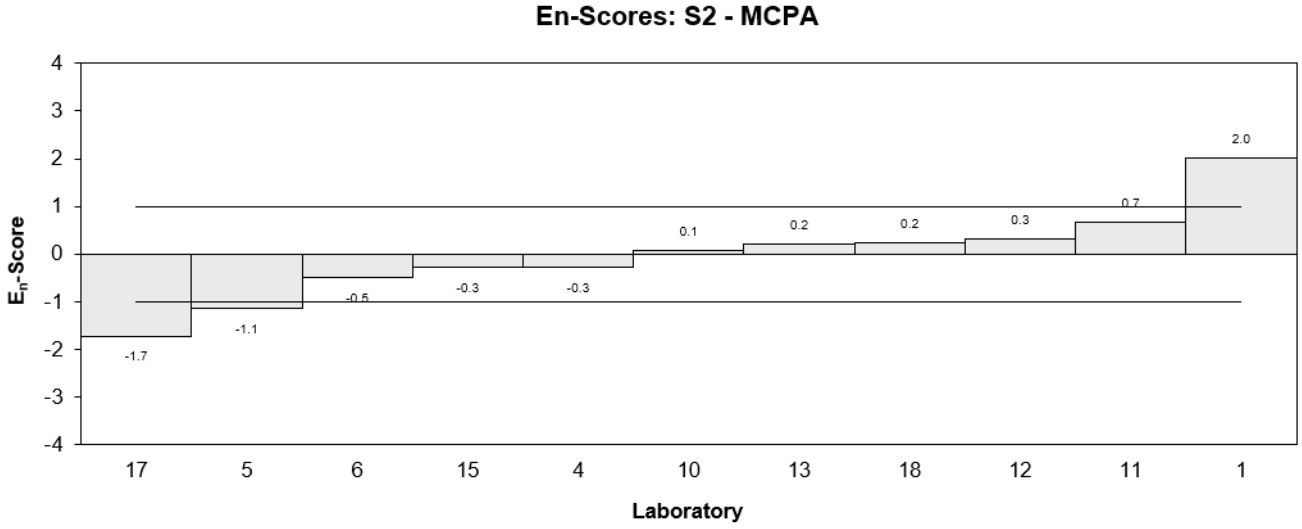

En-Scores: S2 - MCPA
En-Score
Laboratory
17 5 6 15 4 10 13 18 12 11 1
-1.7 -1.1 -0.5 -0.3 -0.3 0.1 0.2 0.2 0.3 0.7 2.0

Figure 18

Table 24

Sample Details

Sample No.	S2
Matrix	Potable Water
Analyte	Total Metolachlor
Unit	mg/L

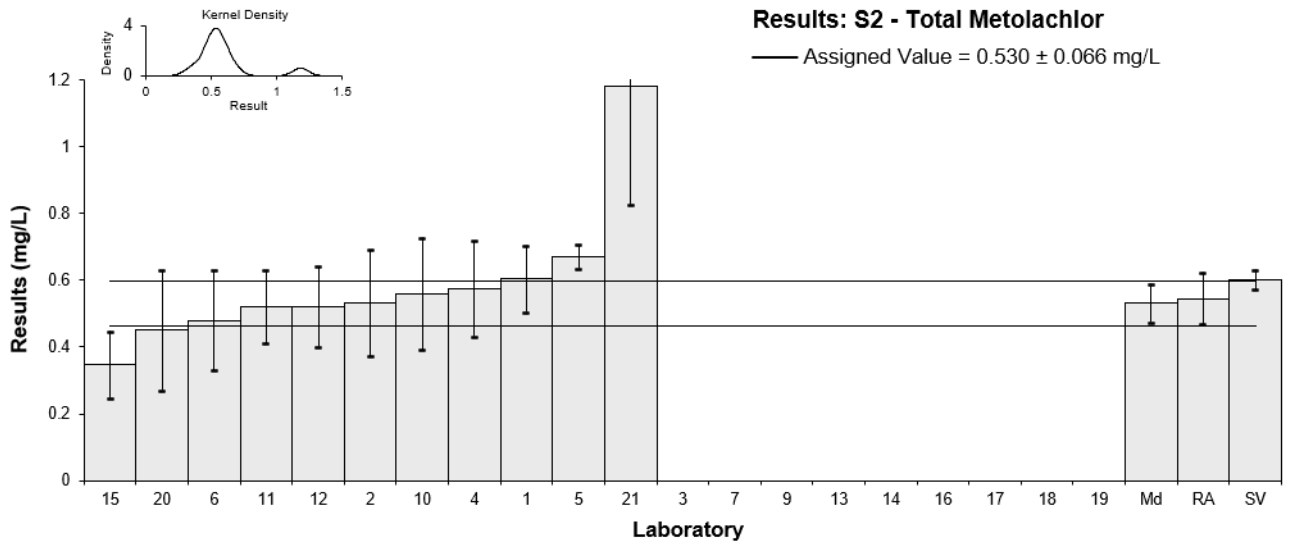
Participant Results

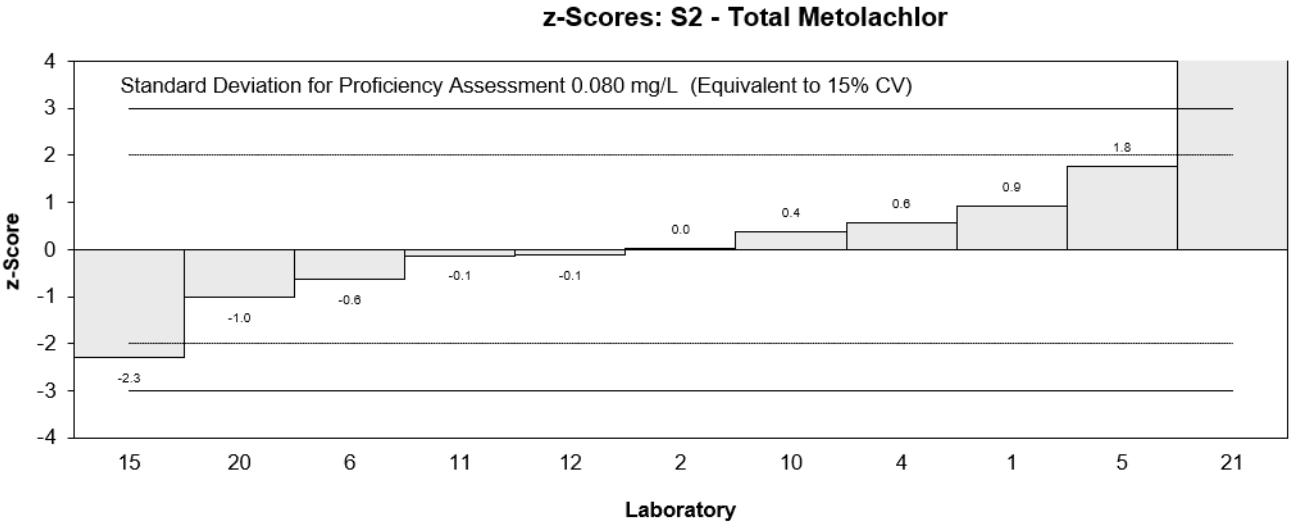
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.604	0.1	NR	0.93	0.62
2	0.5318	0.16	NR	0.02	0.01
3	NT	NT	NT		
4	0.575	0.144	95	0.57	0.28
5	0.671	0.03583	99.04	1.77	1.88
6	0.48	0.15	NR	-0.63	-0.31
7	NT	NT	NT		
9	NS	NS	NS		
10	0.56	0.1680	NR	0.38	0.17
11	0.52	0.11	NR	-0.13	-0.08
12	0.521	0.12	87	-0.11	-0.07
13	NT	NT	NT		
14	NT	NT	NT		
15	0.3478	0.1	NR	-2.29	-1.52
16	NT	NT	NT		
17	NT	NT	NT		
18	NT	NT	NT		
19	NT	NT	NT		
20	0.45	0.18	NR	-1.01	-0.42
21*	1.1823	0.355	NR	8.21	1.81

* Outlier, see Section 4.2

Statistics

Assigned Value	0.530	0.066
Spike Value	0.602	0.030
Robust Average	0.546	0.078
Median	0.532	0.058
Mean	0.59	
N	11	
Max	1.1823	
Min	0.3478	
Robust SD	0.1	
Robust CV	19%	


Kernel Density
Density
Result
Results: S2 - Total Metolachlor
Assigned Value = 0.530 ± 0.066 mg/L
Results (mg/L)
Laboratory
15 20 6 11 12 2 10 4 1 5 21 3 7 9 13 14 16 17 18 19 Md RA SV


z-Scores: S2 - Total Metolachlor
Standard Deviation for Proficiency Assessment 0.080 mg/L (Equivalent to 15% CV)
z-Score
-2.3
-1.0
-0.6
-0.1
-0.1
0.0
0.4
0.6
0.9
1.8
Laboratory
15 20 6 11 12 2 10 4 1 5 21

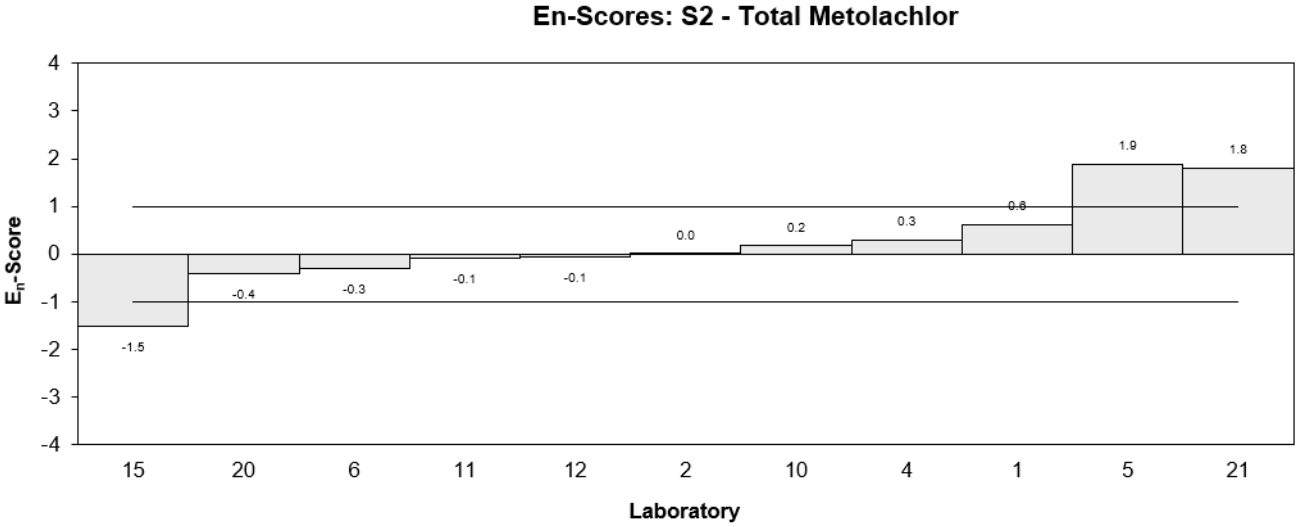

En-Scores: S2 - Total Metolachlor
En-Score
-1.5
-0.4
-0.3
-0.1
-0.1
0.0
0.2
0.3
0.6
1.9
1.8
Laboratory
15 20 6 11 12 2 10 4 1 5 21

Figure 19

Table 25

Sample Details

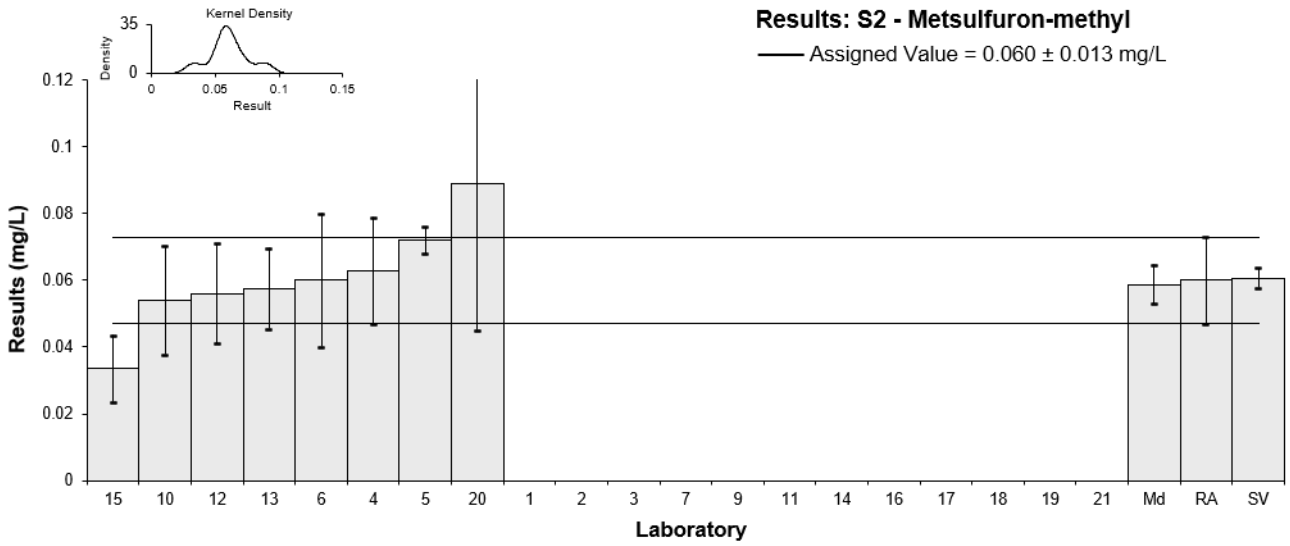
Sample No.	S2
Matrix	Potable Water
Analyte	Metsulfuron-methyl
Unit	mg/L

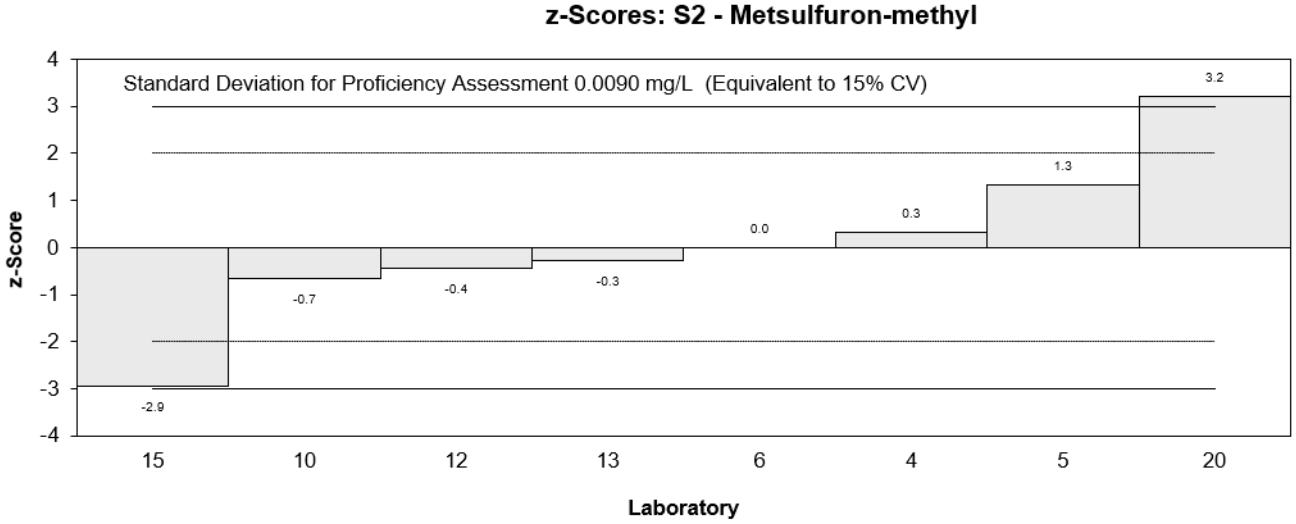
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	NT	NT	NT		
2	NT	NT	NT		
3	NT	NT	NT		
4	0.063	0.016	96	0.33	0.15
5	0.072	0.00412	101.16	1.33	0.88
6	0.06	0.02	NR	0.00	0.00
7	NT	NT	NT		
9	NS	NS	NS		
10	0.054	0.0162	NR	-0.67	-0.29
11	NT	NT	NT		
12	0.056	0.015	71	-0.44	-0.20
13	0.0575	0.0121	NR	-0.28	-0.14
14	NT	NT	NT		
15	0.0335	0.01	NR	-2.94	-1.62
16	NT	NT	NT		
17	NT	NT	NT		
18	NT	NT	NT		
19	NT	NT	NT		
20	0.089	0.044	NR	3.22	0.63
21	NT	NT	NT		

Statistics

Assigned Value	0.060	0.013
Spike Value	0.0607	0.0030
Robust Average	0.060	0.013
Median	0.0588	0.0059
Mean	0.061	
N	8	
Max	0.089	
Min	0.0335	
Robust SD	0.015	
Robust CV	24%	


Kernel Density
Density
Result
Results: S2 - Metsulfuron-methyl
Assigned Value = 0.060 ± 0.013 mg/L
Results (mg/L)
Laboratory
15 10 12 13 6 4 5 20 1 2 3 7 9 11 14 16 17 18 19 21 Md RA SV


z-Scores: S2 - Metsulfuron-methyl
Standard Deviation for Proficiency Assessment 0.0090 mg/L (Equivalent to 15% CV)
z-Score
-2.9
-0.7
-0.4
-0.3
0.0
0.3
1.3
3.2
Laboratory
15 10 12 13 6 4 5 20

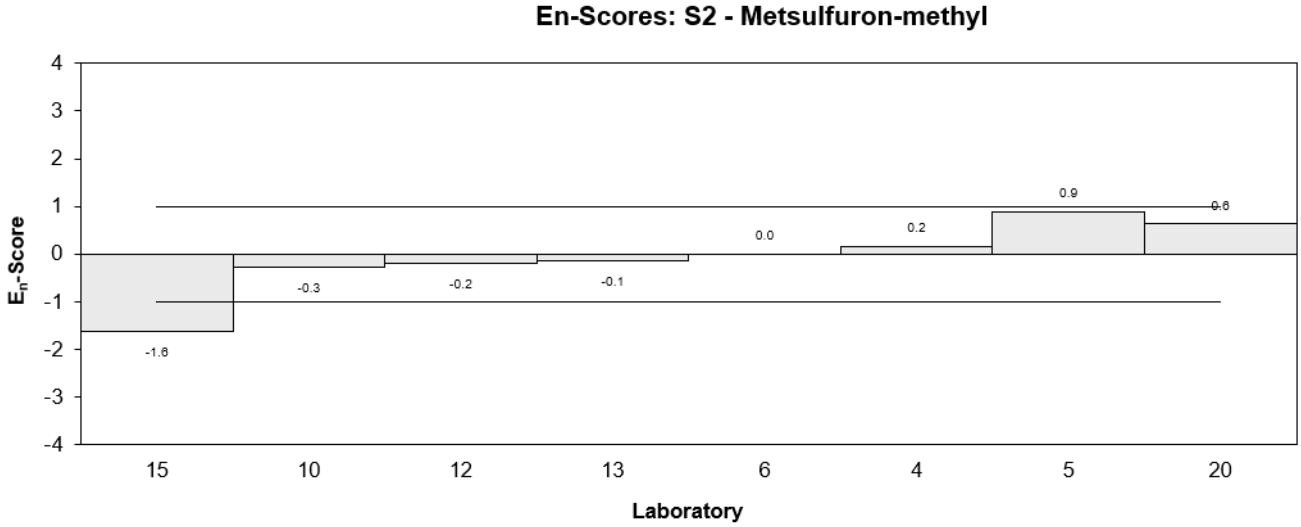

En-Scores: S2 - Metsulfuron-methyl
En-Score
-1.6
-0.3
-0.2
-0.1
0.0
0.2
0.9
0.6
Laboratory
15 10 12 13 6 4 5 20

Figure 20

Table 26

Sample Details

Sample No.	S2
Matrix	Potable Water
Analyte	Picloram
Unit	mg/L

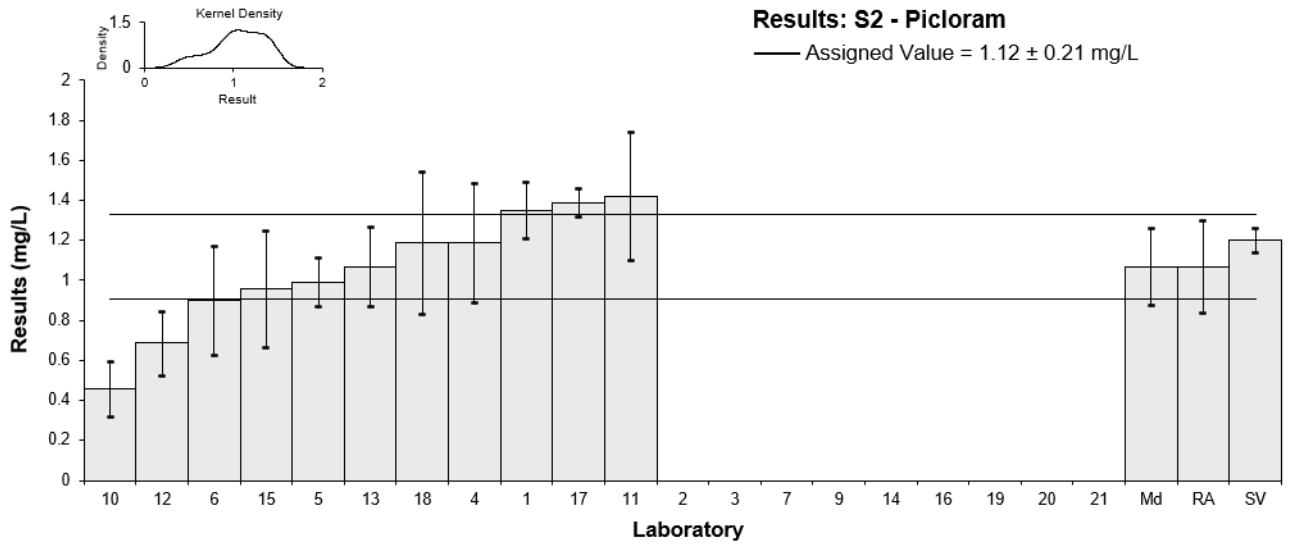
Participant Results

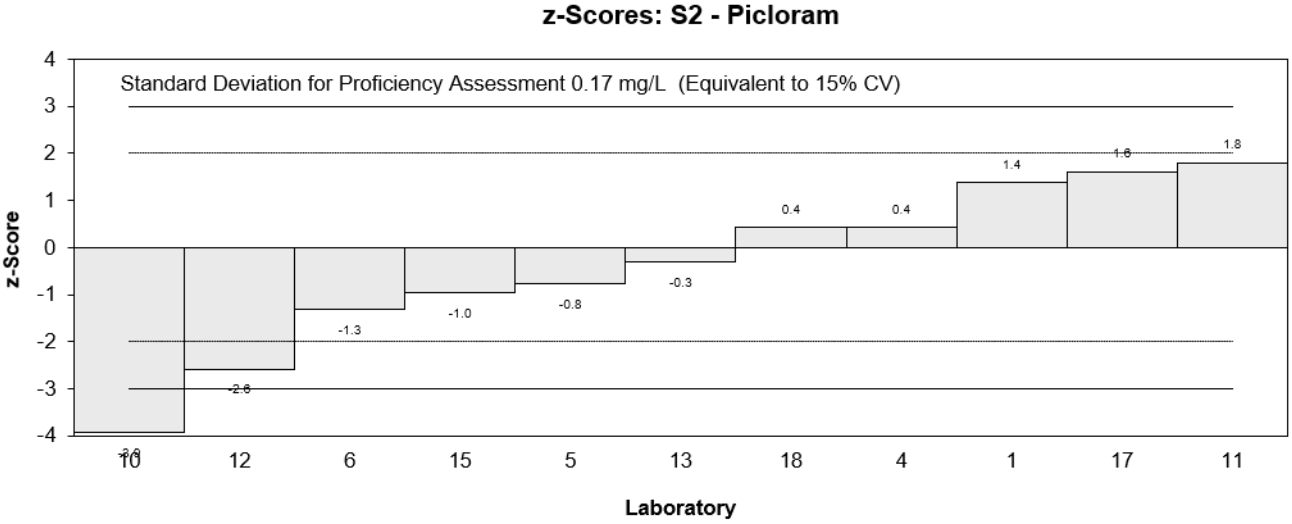
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	1.35	0.14	NR	1.37	0.91
2	NT	NT	NT		
3	NT	NT	NT		
4	1.191	0.298	100	0.42	0.19
5	0.992	0.12013	92.0	-0.76	-0.53
6	0.90	0.27	NR	-1.31	-0.64
7	NT	NT	NT		
9	NS	NS	NS		
10*	0.46	0.138	NR	-3.93	-2.63
11	1.42	0.32	NR	1.79	0.78
12	0.686	0.158	106	-2.58	-1.65
13	1.07	0.20	NR	-0.30	-0.17
14	NT	NT	NT		
15	0.9565	0.29	NR	-0.97	-0.46
16	NT	NT	NT		
17	1.389	0.069	NR	1.60	1.22
18	1.19	0.357	NR	0.42	0.17
19	NT	NT	NT		
20	NT	NT	NT		
21	NT	NT	NT		

* Outlier, see Section 4.2

Statistics

Assigned Value	1.12	0.21
Spike Value	1.20	0.06
Robust Average	1.07	0.23
Median	1.07	0.19
Mean	1.05	
N	11	
Max	1.42	
Min	0.46	
Robust SD	0.31	
Robust CV	29%	


Kernel Density
Density
Result
Results: S2 - Picloram
Assigned Value = 1.12 ± 0.21 mg/L
Results (mg/L)
Laboratory
10 12 6 15 5 13 18 4 1 17 11 2 3 7 9 14 16 19 20 21 Md RA SV


z-Scores: S2 - Picloram
Standard Deviation for Proficiency Assessment 0.17 mg/L (Equivalent to 15% CV)
z-Score
-4.0
-2.6
-1.3
-1.0
-0.8
-0.3
0.4
0.4
1.4
1.6
1.8
Laboratory
10 12 6 15 5 13 18 4 1 17 11

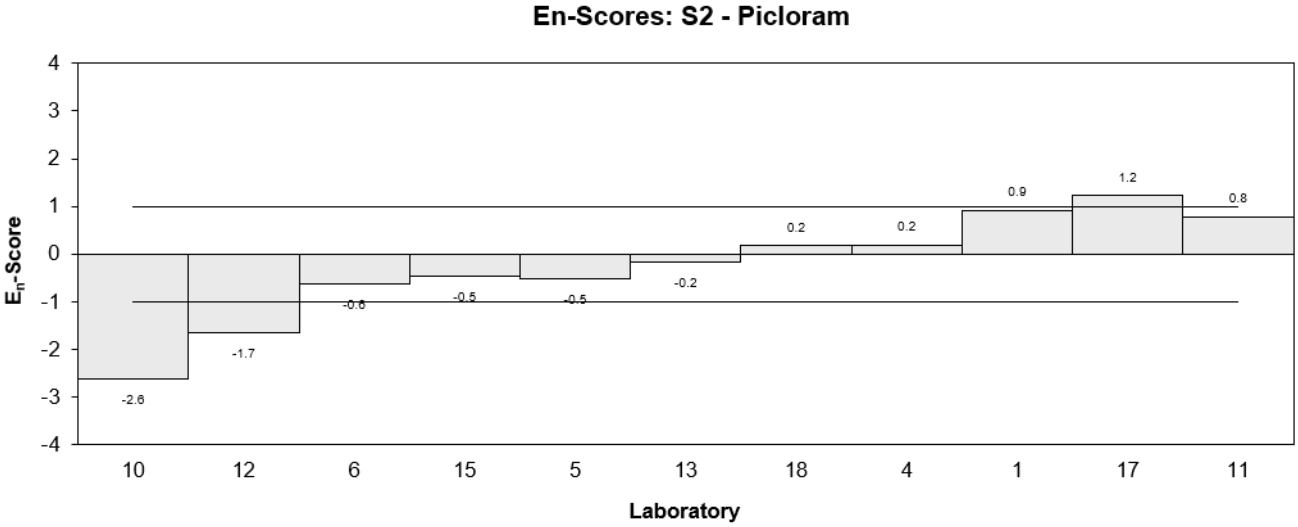

En-Scores: S2 - Picloram
En-Score
-2.6
-1.7
-0.6
-0.5
-0.5
-0.2
0.2
0.2
0.9
1.2
0.8
Laboratory
10 12 6 15 5 13 18 4 1 17 11

Figure 21

Table 27

Sample Details

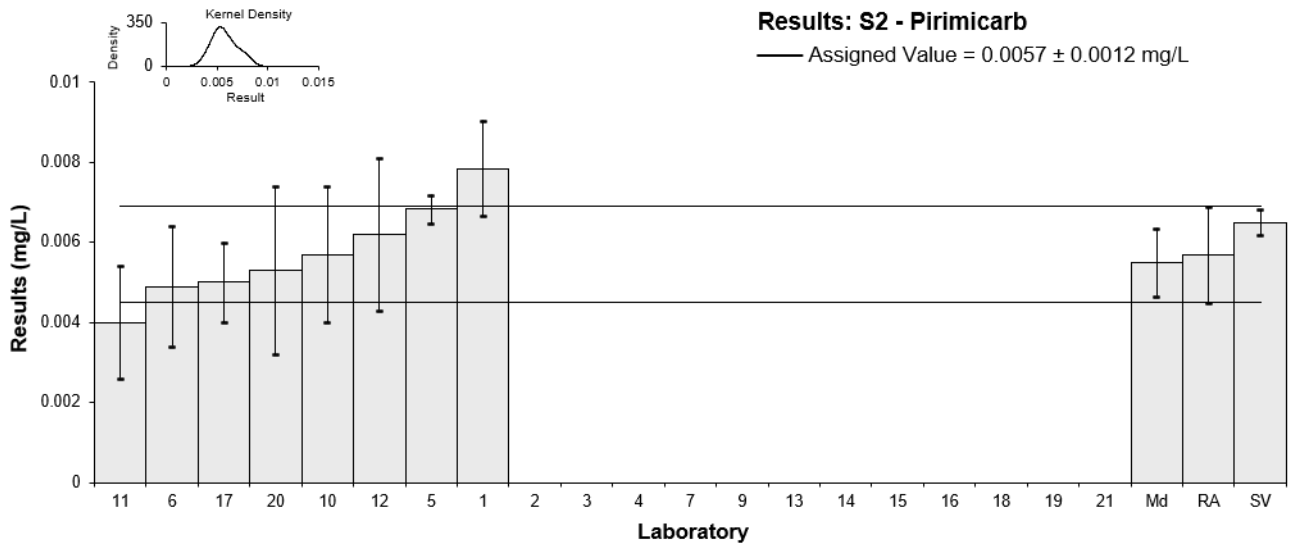
Sample No.	S2
Matrix	Potable Water
Analyte	Pirimicarb
Unit	mg/L

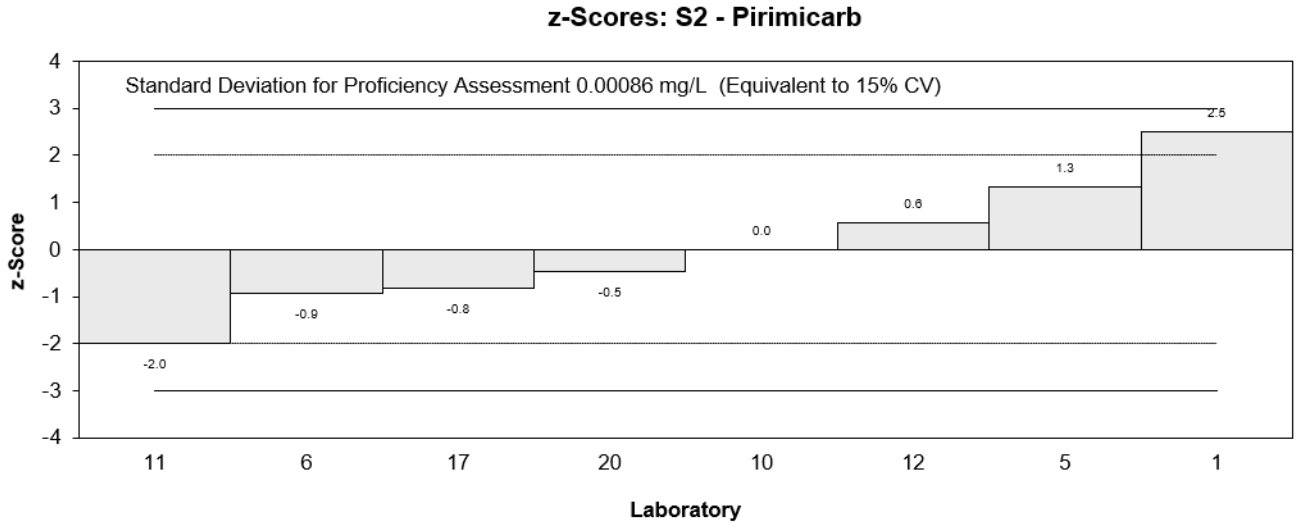
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.00785	0.0012	NR	2.51	1.27
2	NT	NT	NT		
3	NT	NT	NT		
4	NT	NT	NT		
5	0.00683	0.00036	98.53	1.32	0.90
6	0.0049	0.0015	NR	-0.94	-0.42
7	NT	NT	NT		
9	NS	NS	NS		
10	0.0057	0.0017	NR	0.00	0.00
11	0.004	0.0014	NR	-1.99	-0.92
12	0.0062	0.0019	NR	0.58	0.22
13	NT	NT	NT		
14	NT	NT	NT		
15	NT	NT	NT		
16	NT	NT	NT		
17	0.005	0.001	NR	-0.82	-0.45
18	NT	NT	NT		
19	NT	NT	NT		
20	0.0053	0.0021	NR	-0.47	-0.17
21	NT	NT	NT		

Statistics

Assigned Value	0.0057	0.0012
Spike Value	0.00649	0.00032
Robust Average	0.0057	0.0012
Median	0.00550	0.00085
Mean	0.00572	
N	8	
Max	0.00785	
Min	0.004	
Robust SD	0.0013	
Robust CV	23%	


Kernel Density
Density
350
0
0
0.005
0.01
0.015
Result
Results: S2 - Pirimicarb
Assigned Value = 0.0057 ± 0.0012 mg/L
Results (mg/L)
0.01
0.008
0.006
0.004
0.002
0
11 6 17 20 10 12 5 1 2 3 4 7 9 13 14 15 16 18 19 21 Md RA SV
Laboratory


z-Scores: S2 - Pirimicarb
Standard Deviation for Proficiency Assessment 0.00086 mg/L (Equivalent to 15% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-2.0
-0.9
-0.8
-0.5
0.0
0.6
1.3
2.5
11 6 17 20 10 12 5 1
Laboratory

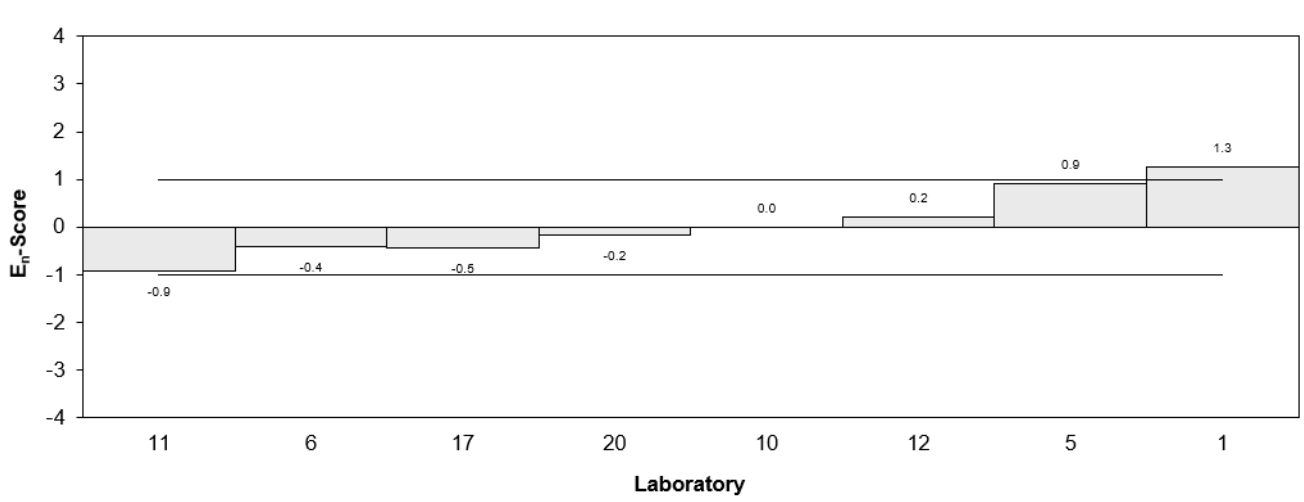

En-Scores: S2 - Pirimicarb
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.9
-0.4
-0.5
-0.2
0.0
0.2
0.9
1.3
11 6 17 20 10 12 5 1
Laboratory

Figure 22

Table 28

Sample Details

Sample No.	S2
Matrix	Potable Water
Analyte	Propazine
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	0.000184	0.00004	NR
2	<0.00005	NR	NR
3	NT	NT	NT
4	0.000155	0.000039	94
5	NT	NT	NT
6	0.00016	0.00008	NR
7	NT	NT	NT
9	NS	NS	NS
10	< 0.0001	NR	NR
11	<0.00009	0.000029	NR
12	0.00016	0.00006	117
13	NT	NT	NT
14	NT	NT	NT
15	< 0.002	NR	NR
16	NT	NT	NT
17	<0.002	NR	NR
18	NT	NT	NT
19	NT	NT	NT
20	<0.001	NR	NR
21	<0.00005	NR	NR

Statistics

Assigned Value	Not Set	
Spike Value	Not Spiked	
Robust Average	NA (N<6)	
Median	0.000160	0.000005
Mean	0.000165	
N	4	
Max	0.000184	
Min	0.000155	
Robust SD	NA (N<6)	
Robust CV	NA (N<6)	

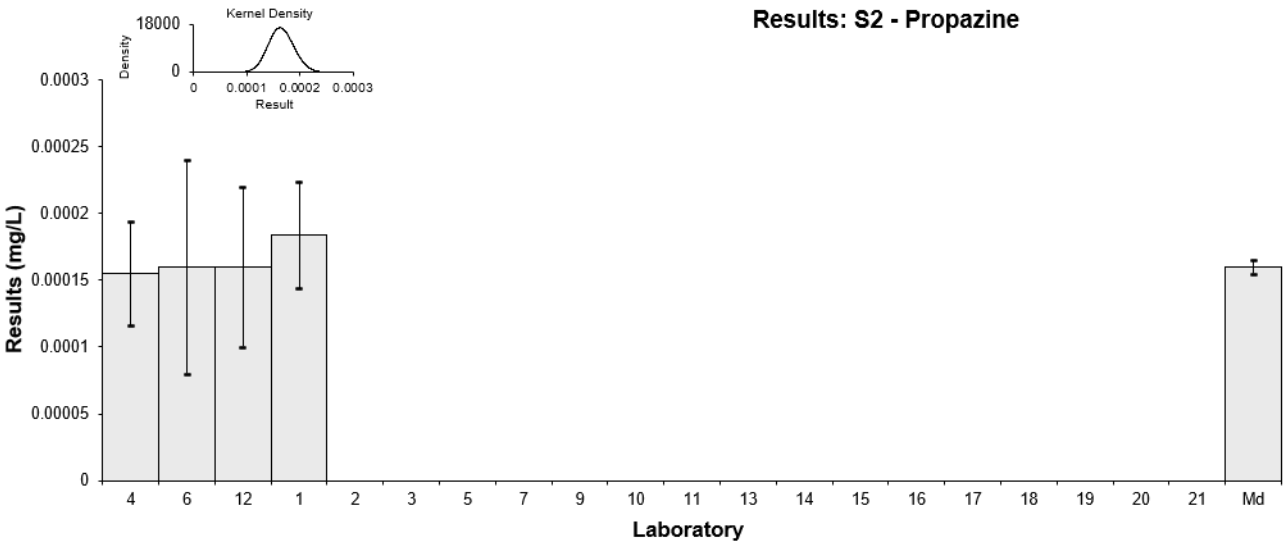

Results: S2 - Propazine
Kernel Density
Density
18000
0
0
0.0001
0.0002
0.0003
Result
Results (mg/L)
0.0003
0.00025
0.0002
0.00015
0.0001
0.00005
0
4
6
12
1
2
3
5
7
9
10
11
13
14
15
16
17
18
19
20
21
Md
Laboratory

Figure 23

Table 29

Sample Details

Sample No.	S2
Matrix	Potable Water
Analyte	Triadimefon
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	NT	NT	NT
2	NT	NT	NT
3	NT	NT	NT
4	NT	NT	NT
5	0.0925	0.00481	97.14
6	0.087	0.03	NR
7	NT	NT	NT
9	NS	NS	NS
10	0.054	0.0162	NR
11	0.0598	0.0048	NR
12	NT	NT	NT
13	NT	NT	NT
14	NT	NT	NT
15	NT	NT	NT
16	NT	NT	NT
17	0.102	0.015	NR
18	NT	NT	NT
19	NT	NT	NT
20	0.098	0.049	NR
21	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	0.0900	0.0045
Robust Average	0.082	0.024
Median	0.090	0.016
Mean	0.082	
N	6	
Max	0.102	
Min	0.054	
Robust SD	0.023	
Robust CV	28%	

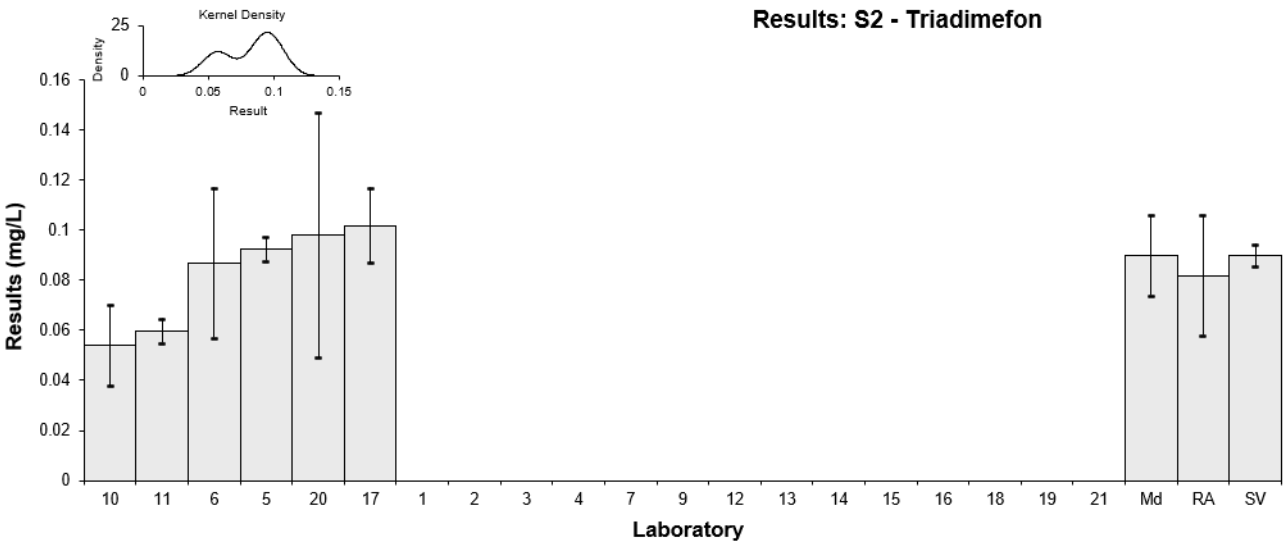

Results: S2 - Triadimefon
Kernel Density
Density
25
0
0
0.05
0.1
0.15
Result
Results (mg/L)
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
10
11
6
5
20
17
1
2
3
4
7
9
12
13
14
15
16
18
19
21
Md
RA
SV
Laboratory

Figure 24

Table 30

Sample Details

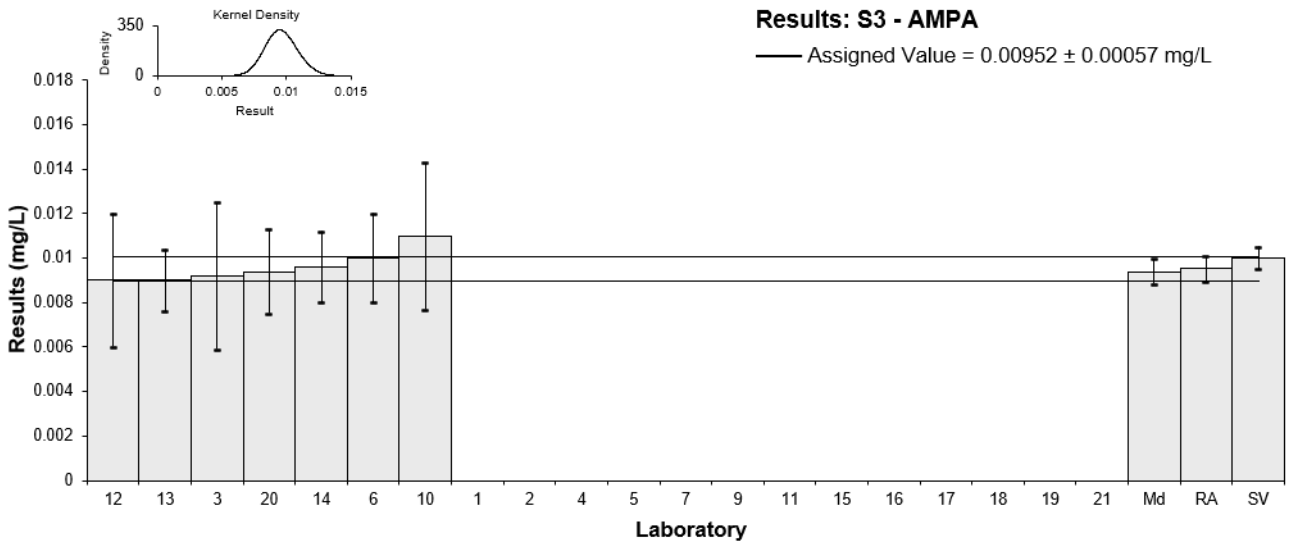
Sample No.	S3
Matrix	Potable Water
Analyte	AMPA
Unit	mg/L

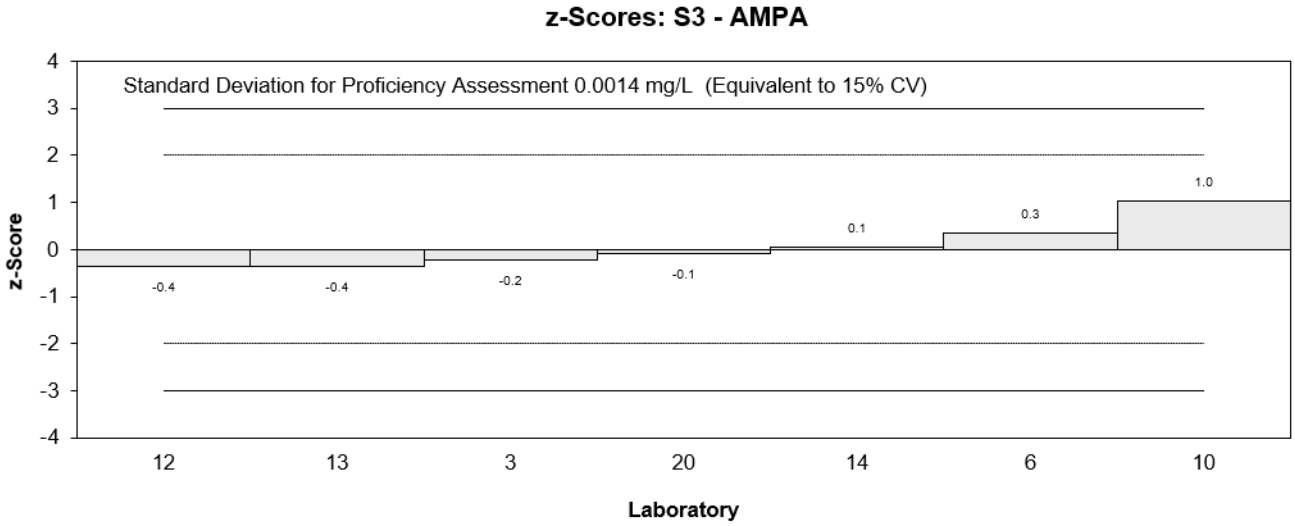
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	NT	NT	NT		
2	NS	NS	NS		
3	0.0092	0.0033	78	-0.22	-0.10
4	NT	NT	NT		
5	NT	NT	NT		
6	0.010	0.002	NR	0.34	0.23
7	NS	NS	NS		
9	NS	NS	NS		
10	0.011	0.0033	NR	1.04	0.44
11	NT	NT	NT		
12	0.009	0.003	88	-0.36	-0.17
13	0.009	0.0014	NR	-0.36	-0.34
14	0.0096	0.0016	100	0.06	0.05
15	NS	NS	NS		
16	NT	NT	NT		
17	<0.1	NR	NR		
18	NS	NS	NS		
19	NS	NS	NS		
20	0.0094	0.0019	100	-0.08	-0.06
21	NS	NS	NS		

Statistics

Assigned Value	0.00952	0.00057
Spike Value	0.0100	0.0005
Robust Average	0.00952	0.00057
Median	0.00940	0.00056
Mean	0.00960	
N	7	
Max	0.011	
Min	0.009	
Robust SD	0.00060	
Robust CV	6.3%	


Kernel Density
Density
350
0
0
0.005
0.01
0.015
Result
Results: S3 - AMPA
Assigned Value = 0.00952 ± 0.00057 mg/L
Results (mg/L)
0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
12 13 3 20 14 6 10 1 2 4 5 7 9 11 15 16 17 18 19 21 Md RA SV
Laboratory


z-Scores: S3 - AMPA
Standard Deviation for Proficiency Assessment 0.0014 mg/L (Equivalent to 15% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-0.4
-0.4
-0.2
-0.1
0.1
0.3
1.0
12 13 3 20 14 6 10
Laboratory

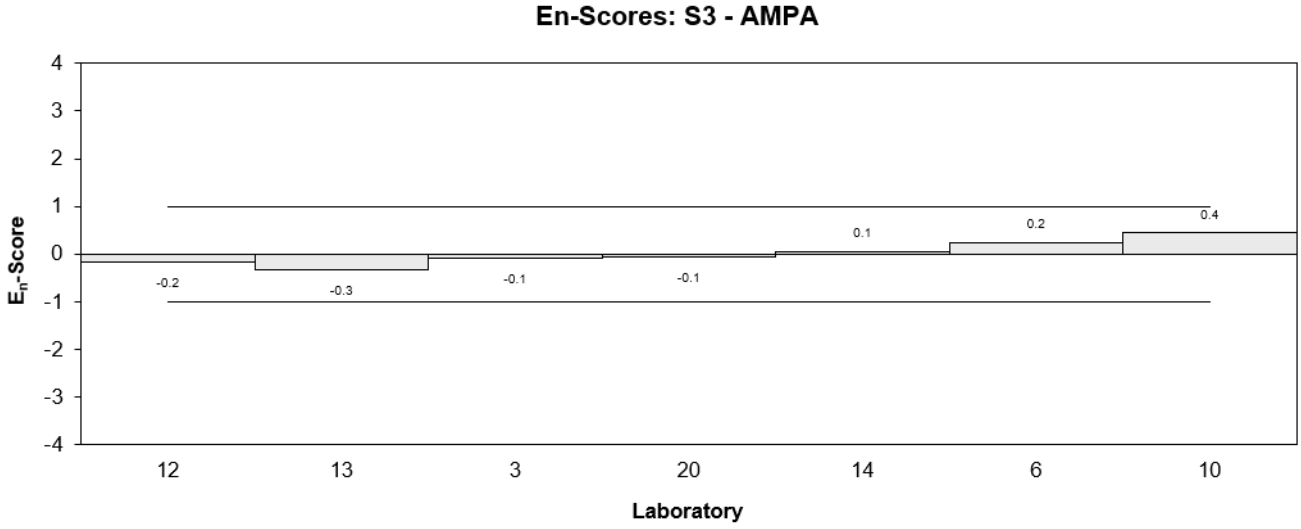

En-Scores: S3 - AMPA
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.2
-0.3
-0.1
-0.1
0.1
0.2
0.4
12 13 3 20 14 6 10
Laboratory

Figure 25

Table 31

Sample Details

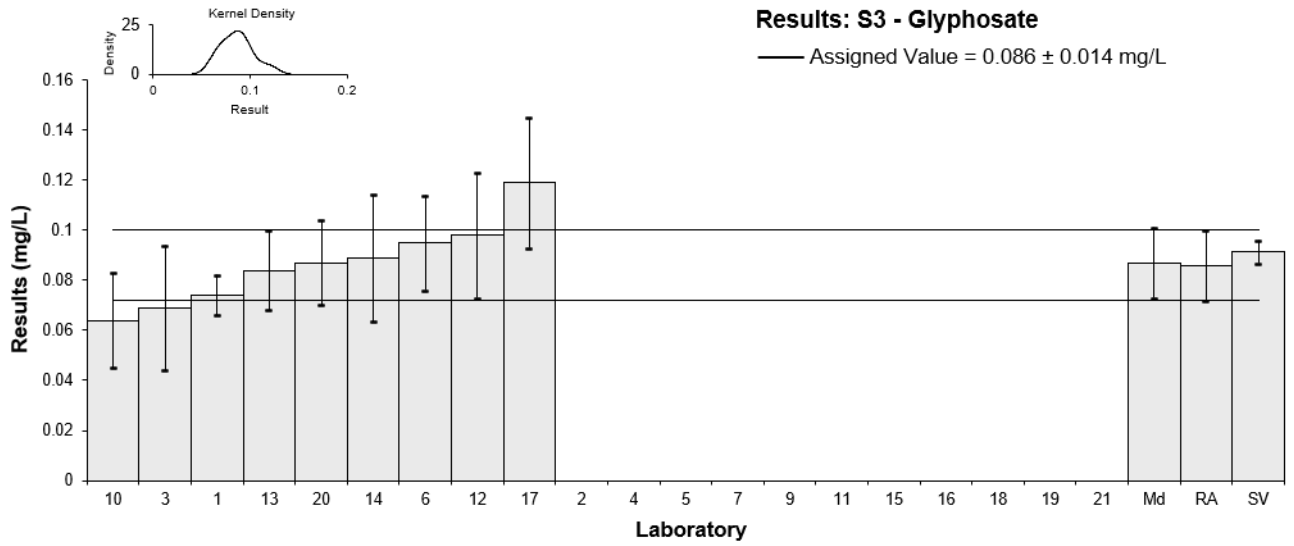
Sample No.	S3
Matrix	Potable Water
Analyte	Glyphosate
Unit	mg/L

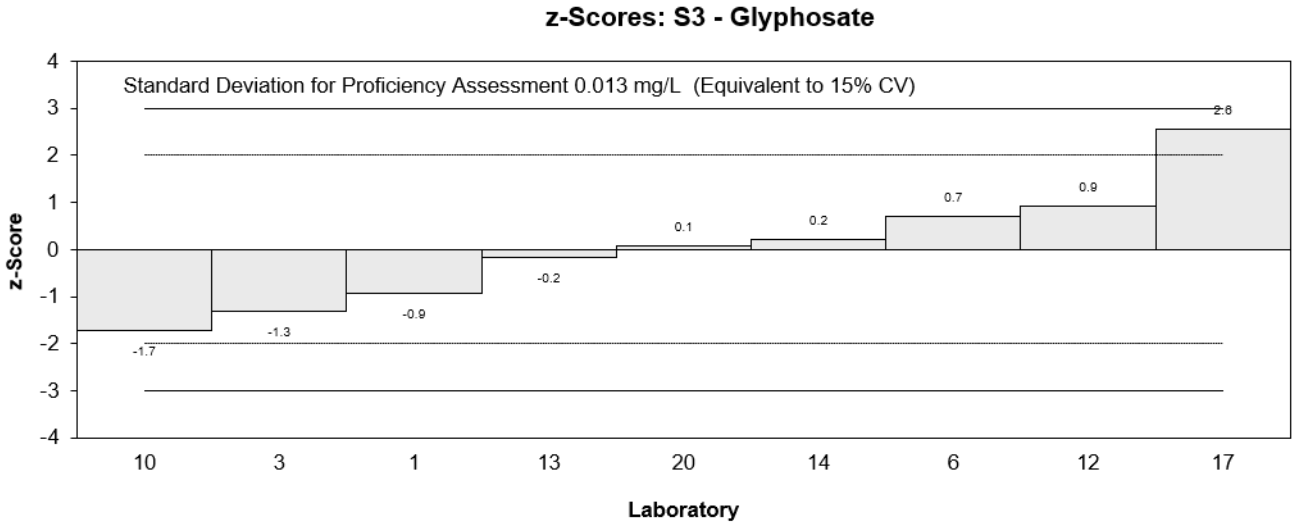
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.0741	0.008	NR	-0.92	-0.74
2	NS	NS	NS		
3	0.069	0.025	117	-1.32	-0.59
4	NT	NT	NT		
5	NT	NT	NT		
6	0.095	0.019	NR	0.70	0.38
7	NS	NS	NS		
9	NS	NS	NS		
10	0.064	0.019	NR	-1.71	-0.93
11	NT	NT	NT		
12	0.098	0.025	92	0.93	0.42
13	0.084	0.016	NR	-0.16	-0.09
14	0.0888	0.0254	109	0.22	0.10
15	NS	NS	NS		
16	NT	NT	NT		
17	0.119	0.026	NR	2.56	1.12
18	NS	NS	NS		
19	NS	NS	NS		
20	0.087	0.017	20	0.08	0.05
21	NS	NS	NS		

Statistics

Assigned Value	0.086	0.014
Spike Value	0.0914	0.0046
Robust Average	0.086	0.014
Median	0.087	0.014
Mean	0.087	
N	9	
Max	0.119	
Min	0.064	
Robust SD	0.017	
Robust CV	20%	


Kernel Density
Density
Result
Results: S3 - Glyphosate
Assigned Value = 0.086 ± 0.014 mg/L
Results (mg/L)
Laboratory
10 3 1 13 20 14 6 12 17 2 4 5 7 9 11 15 16 18 19 21 Md RA SV


z-Scores: S3 - Glyphosate
Standard Deviation for Proficiency Assessment 0.013 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
10 3 1 13 20 14 6 12 17
-1.7 -1.3 -0.9 -0.2 0.1 0.2 0.7 0.9 2.6

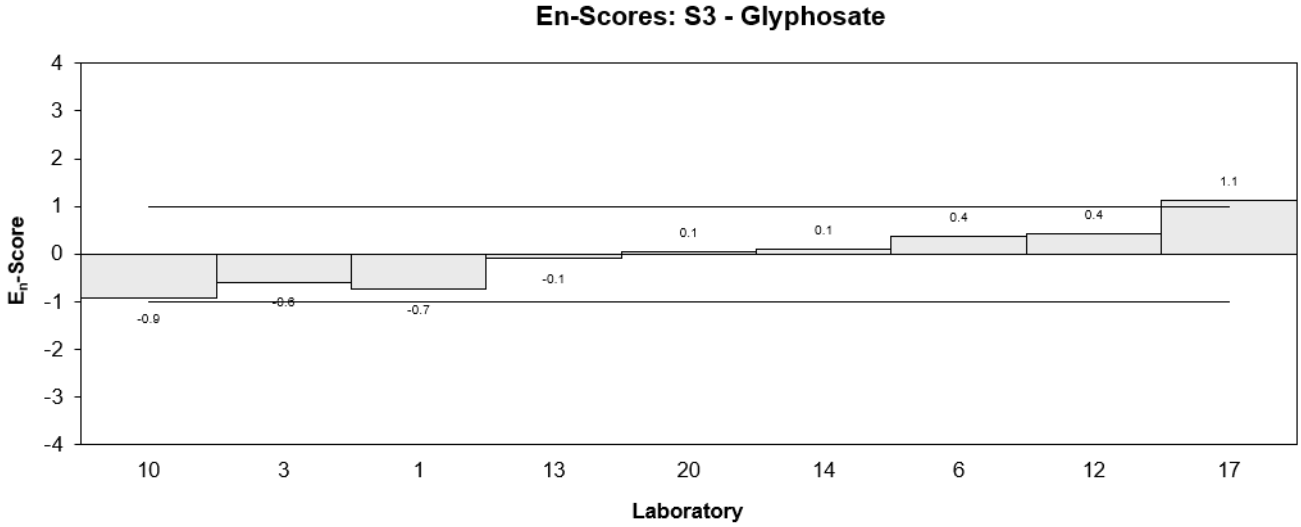

En-Scores: S3 - Glyphosate
En-Score
Laboratory
10 3 1 13 20 14 6 12 17
-0.9 -0.6 -0.7 -0.1 0.1 0.1 0.4 0.4 1.1

Figure 26

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The assigned values for all scored analytes were the robust averages of participants' results. Results less than 50% or greater than 150% of the robust average were excluded from the calculation of each assigned value.[3,4] The robust averages and associated expanded uncertainties were calculated using the procedure described in ISO 13528.[6] The calculation of the expanded uncertainty for robust averages is presented in Appendix 3, using MCPA in Sample S2 as an example.

No assigned values were set for azinphos-methyl, total cypermethrin, p,p'-DDT, total endosulfan, maldison, and pirimiphos-methyl in Sample S1, and acephate, atrazine, fipronil, propazine, and triadimefon in Sample S2. This was due to an insufficient number of numeric results, high variability of reported results, and/or poor recovery of the spiked value. Participants may still compare their results for these non-scored analytes with the descriptive statistics and spiked value as presented in Section 5.

The ratios of the assigned values to spiked values are presented in Table 32. For scored analytes, assigned values were within the range of 54% to 106% of the spiked values, which is similar to ratios observed in previous NMIA PT studies.

The significant instability observed for Sample S1 total endosulfan and maldison is discussed in Section 6.8.

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

Table 32 Comparison of Assigned Value and Spiked Value

Sample	Analyte	Assigned Value / Spiked Value (%)
S1	Atrazine	93
S1	Azinphos-methyl	67*
S1	Total Chlordane	54
S1	Total Cypermethrin	82*
S1	p,p'-DDT	58*
S1	Dieldrin	78
S1	Total Endosulfan	6*
S1	Maldison	21*
S1	Picloram	93
S1	Pirimiphos-methyl	45*
S1	Total Propiconazole	77
S2	Acephate	78*
S2	Atrazine	88*
S2	Bromacil	106
S2	2,4-D	106
S2	Fipronil	89*
S2	MCPA	101
S2	Total Metolachlor	88

Sample	Analyte	Assigned Value / Spiked Value (%)
S2	Metsulfuron-methyl	99
S2	Picloram	93
S2	Pirimicarb	88
S2	Triadimefon	91*
S3	AMPA	95
S3	Glyphosate	94

*Calculated using the robust average or median as applicable (assigned value not set).

6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an evaluation of the expanded MU associated with their results and the basis of this evaluation. It is a requirement of ISO/IEC 17025 that laboratories have procedures to evaluate and report the uncertainty of chemical measurements.[8]

Of 241 numeric results submitted for the analytes of interest in this study, 240 were reported with an expanded MU. Participants used a wide variety of procedures to evaluate their uncertainty (Tables 4 and 5).

Laboratory 10 did not report an uncertainty for Sample S1 picloram only, however they were accredited to ISO/IEC 17025.

The magnitude of reported relative uncertainties was within the range of 2.6% to 100%. In general, an expanded relative uncertainty of less than 15% may be unrealistically small for routine analysis, while over 50% may be too large to be fit-for-purpose. In this study, 201 (84%) relative uncertainties were between 15% and 50%; 32 relative uncertainties were less than 15%, and 7 relative uncertainties were greater than 50%.

The following participants may need to review the procedure they used to evaluate their uncertainties, or review if an error was made when reporting:

- Laboratory 3 reported relative uncertainties ranging from 29% to 36% for all analytes except for Sample S1 azinphos-methyl where they reported a relative uncertainty of 3%.
- Laboratory 5 reported relative uncertainties all less than 15%, which may be unrealistically small for routine analysis.
- Laboratory 16 reported relative uncertainties all greater than 50%, including an expanded uncertainty equal to the result itself, which may be too large to be fit-for-purpose.

Participants were requested to report the coverage factor associated with their uncertainties (Table 4). Most participants reported using a coverage factor of $k = 2$.

Uncertainties associated with results returning an acceptable z-score but a not acceptable E_n-score may have been underestimated.

Laboratory 9, 11, and 16 attached evaluations of expanded MU to results reported as less than their limit of reporting. An evaluation of uncertainty expressed as a value cannot be attached to a result expressed as a range.[9]

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 2 significant figures and then write the result with the corresponding number of decimal places. For example, instead of 0.0337 ± 0.0106 mg/L, report this as 0.034 ± 0.011 mg/L.[9]

6.3 z-Score

The z-score compares the participant's deviation from the assigned value based on the standard deviation for proficiency assessment (SDPA). The SDPA defines acceptable performance in a PT study. SDPAs equivalent to 15% PCV were used to calculate z-scores in this study. Unlike the standard deviation based on between-laboratory CV, setting the SDPA as a realistic value enables z-scores to be used as reference value points for assessment of individual laboratory performance, independent of the group's performance.

Table 33 presents the CVs predicted by the Thompson-Horwitz equation, the between-laboratory CVs, and SDPAs (as PCVs) for scored analytes.[7] Table 34 presents the CVs predicted by the Thompson-Horwitz equation and the between-laboratory CVs for non-scored analytes.[7]

Table 33 Comparison of Between-Laboratory CVs, Thompson-Horwitz CVs, and SDPAs for Scored Analytes

Sample	Analyte	Numeric Results Reported*	Assigned Value (mg/L)	Between-Laboratory CV* (%)	Thompson-Horwitz CV (%)	SDPA (as PCV, %)
S1	Atrazine	12	0.0140	14	22	15
S1	Total Chlordane	10	0.00106	22	22	15
S1	Dieldrin	11	0.000276	19	22	15
S1	Picloram	7	0.56	23	17	15
S1	Total Propiconazole	8	0.140	22	22	15
S2	Bromacil	8	0.69	26	17	15
S2	2,4-D	11	0.0426	17	22	15
S2	MCPA	11	0.0401	17	22	15
S2	Total Metolachlor	10	0.530	16	18	15
S2	Metsulfuron-methyl	8	0.060	24	22	15
S2	Picloram	10	1.12	23	16	15
S2	Pirimicarb	8	0.0057	23	22	15
S3	AMPA	7	0.00952	6.3	22	15
S3	Glyphosate	9	0.086	20	22	15

*Values exclude outliers if applicable. Shaded cells represent between-laboratory CVs higher than both the SDPA and the Thompson-Horwitz CV.

Table 34 Comparison of Between-Laboratory CVs and Thompson-Horwitz CVs for Non-Scored Analytes

Sample	Analyte	Numeric Results Reported	Consensus Value* (mg/L)	Between-Laboratory CV (%)	Thompson-Horwitz CV (%)
S1	Azinphos-methyl	16	0.0267	42	22
S1	Total Cypermethrin	7	0.33	75	19
S1	p,p'-DDT	14	0.0048	66	22
S1	Total Endosulfan	11	0.0018	127	22
S1	Maldison	8	0.032	71	22

Sample	Analyte	Numeric Results Reported	Consensus Value* (mg/L)	Between-Laboratory CV (%)	Thompson-Horwitz CV (%)
S1	Pirimiphos-methyl	10	0.068	22	22
S2	Acephate	3	0.0077	12	22
S2	Atrazine	14	0.0222	36	22
S2	Fipronil	6	0.00131	31	22
S2	Propazine	4	0.000160	2.3	22
S2	Triadimefon	6	0.082	28	22

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

To account for possible low bias in consensus values due to participants using inefficient extraction or analytical techniques, a total of 2 z-scores were adjusted across the following analytes: Sample S1 total chlordane and total propiconazole. A maximum acceptable result was set as the spiked value plus 2 SDPAs of the spiked value. Results lower than the maximum acceptable result but with a z-score greater than 2.0 had their z-score adjusted to 2.0. This ensured that participants reporting results close to the spiked value were not penalised. z-Scores for results higher than the maximum acceptable result and z-scores less than 2.0 were left unaltered.

Of 139 results for which z-scores were calculated, 122 (88%) returned a score of $|z| \leq 2.0$, indicating an acceptable performance.

Laboratories 6, 10, and 12 reported numeric results for all 14 scored analytes. Of these participants, Laboratory 6 returned acceptable z-scores for all analytes.

Eight other participants received acceptable z-scores for all analytes they reported results for: Laboratories 5 (9), 13 (9), 4 (8), 3 (4), 18 (4), 14 (3), 7 (2), and 19 (2).

Laboratory 16 and 21 reported numeric results for only one and 2 scored analytes respectively; neither participant returned any acceptable z-scores.

Laboratory 9 did not report any numeric results for scored analytes in this study and so they did not receive any z-scores.

The dispersal of z-scores is presented by laboratory in Figure 27, and by analyte in Figure 28.

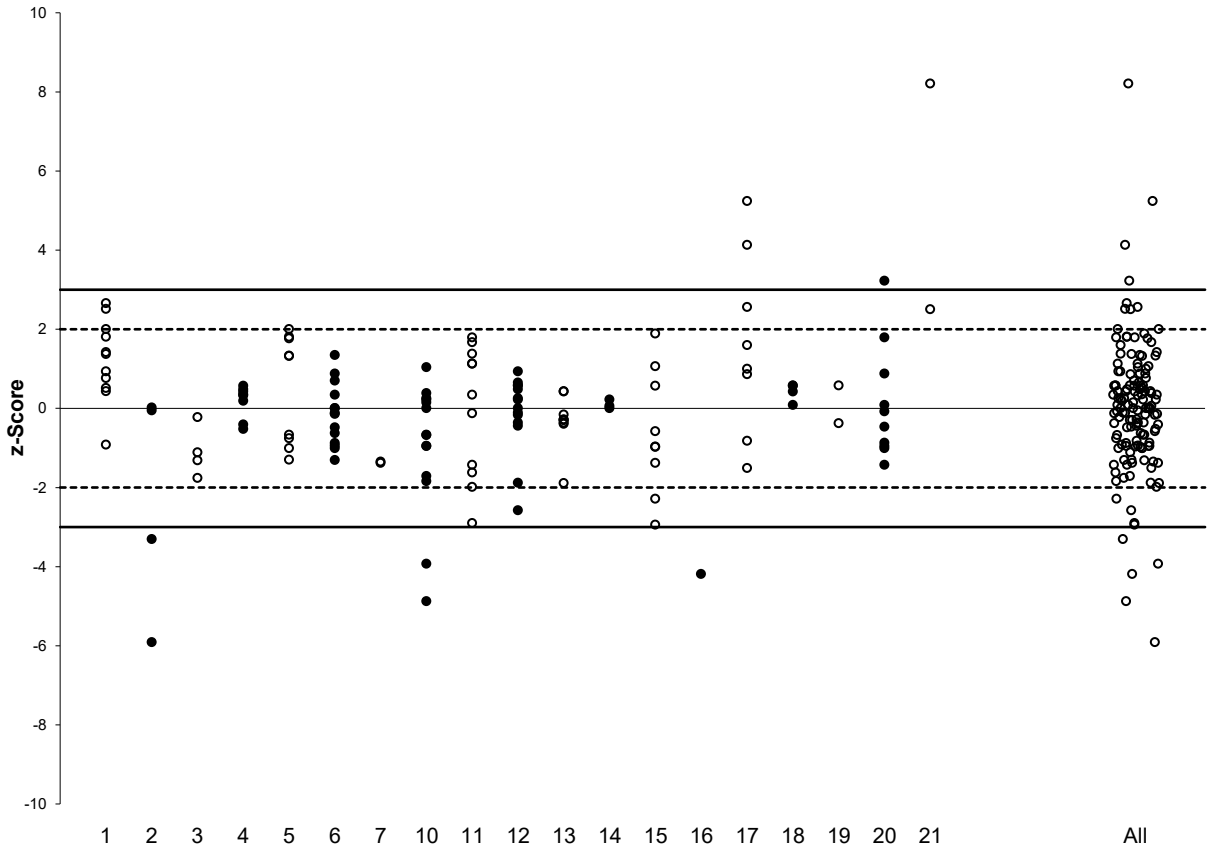


Figure 27 *z*-Score Dispersal by Laboratory

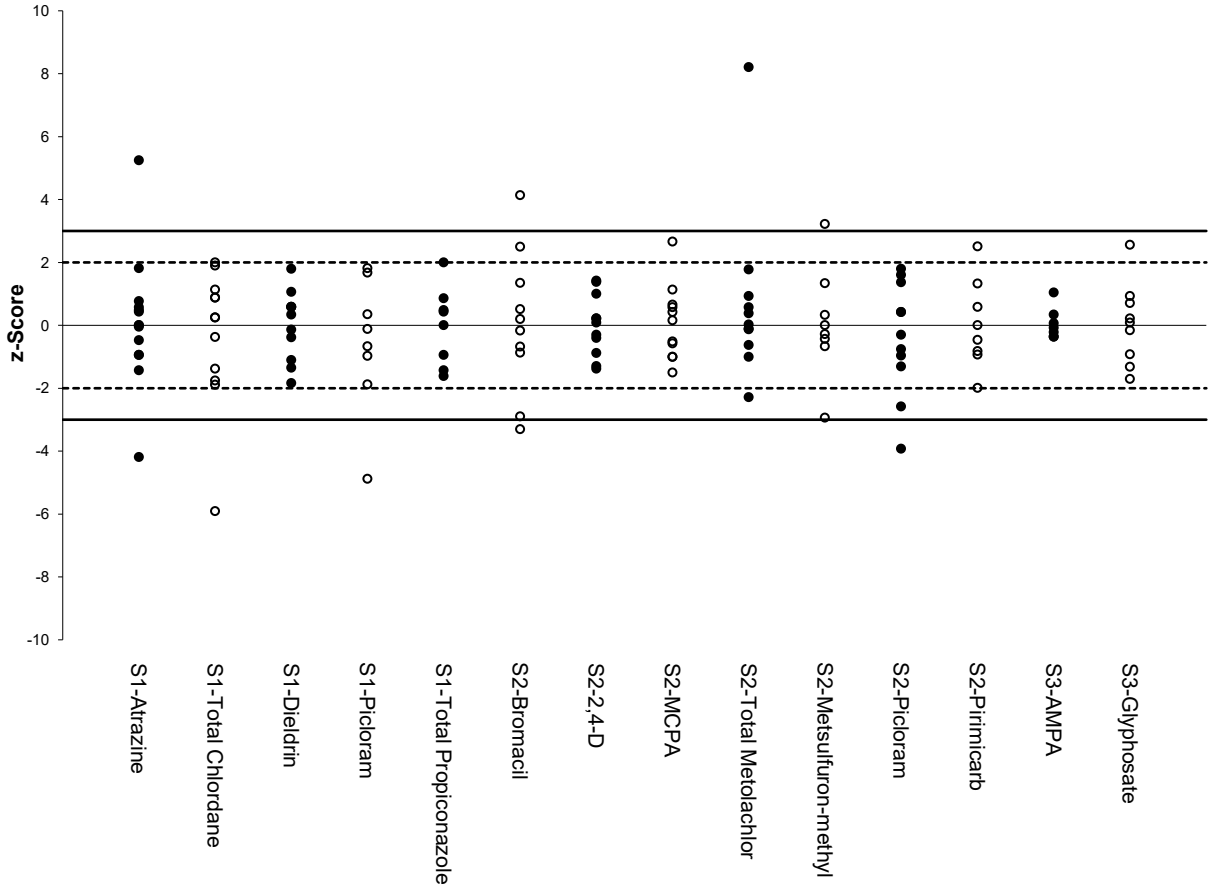


Figure 28 *z*-Score Dispersal by Analyte

6.4 E_n-Score

The E_n-score indicates how closely a result agrees with the assigned value, taking into consideration the respective uncertainties. E_n-Scores can be interpreted in conjunction with z-scores, as a not acceptable E_n-score can either be caused by issue with measurement, an inappropriate evaluation of measurement uncertainty, or both.

Where a participant did not report an uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the E_n-score. For results whose z-scores were adjusted as discussed in Section 6.3, no E_n-score has been calculated.

Of 137 results for which E_n-scores were calculated, 112 (82%) returned an acceptable score of $|E_n| < 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratory 6 returned acceptable E_n-scores for all 14 scored analytes.

Eight other participants received acceptable E_n-scores for all analytes they reported results for: Laboratories 20 (10), 13 (9), 4 (8), 3 (4), 18 (4), 14 (3), 7 (2), and 19 (2).

Laboratory 16 returned a not acceptable E_n-score for the one scored analyte they reported a numeric result for.

The dispersal of E_n-scores by laboratory is presented in Figure 29.

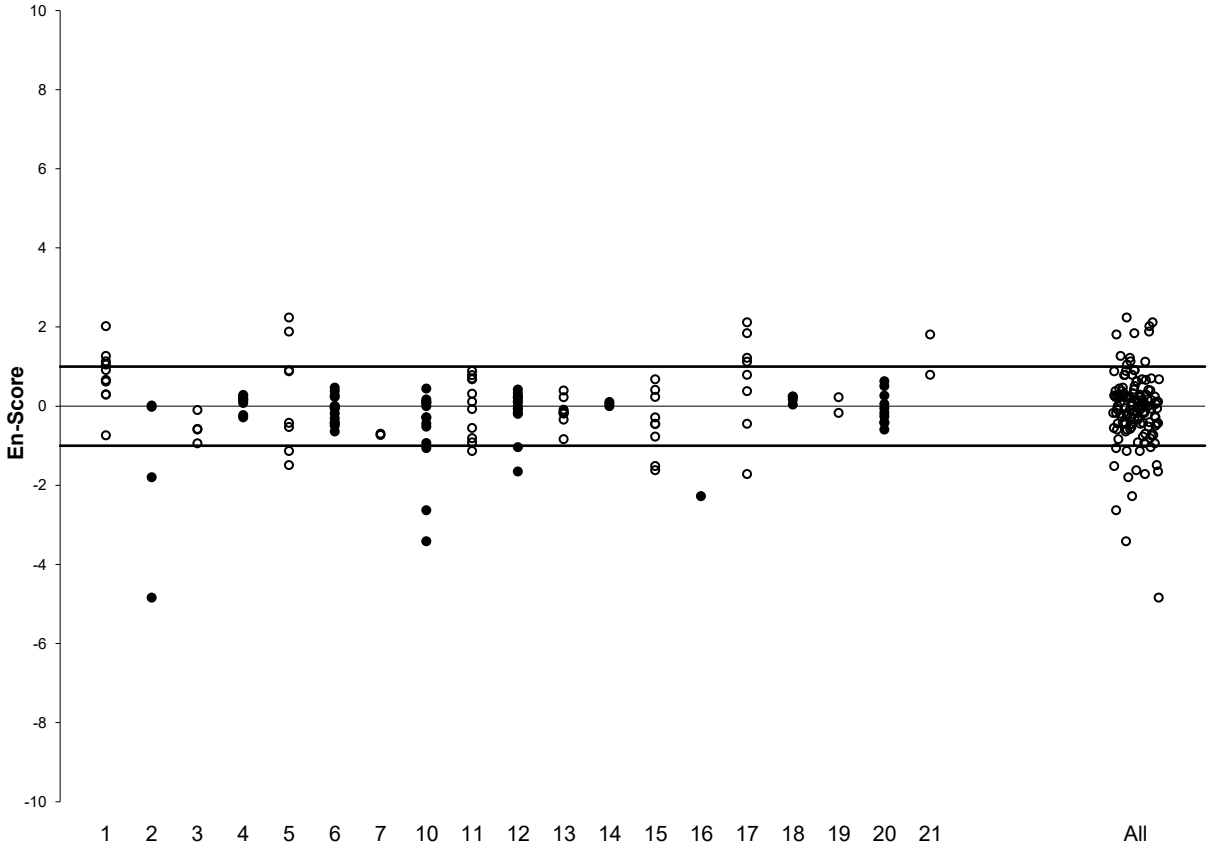


Figure 29 E_n-Score Dispersal by Laboratory

6.5 False Negatives

Table 35 presents false negative results. These are analytes present in the samples which a participant tested for but did not report a numeric result. This includes 'Not Reported' results, or those that were reported as a 'less than' result ($< x$) when the assigned value, less its expanded uncertainty, was greater than the participant's limit of reporting (LOR).

For analytes where no assigned value was set, results have only been considered to be false negatives if no value was reported, or if the consensus value and spiked value, less their respective expanded uncertainties, were both greater than the participants' LOR.

Table 35 False Negatives

Lab. Code	Sample	Analyte	Assigned Value (mg/L)	Consensus Value* (mg/L)	Spiked Value (mg/L)	Result (mg/L)
2	S1	Dieldrin	0.000276	N/A	N/A	<0.00005
2	S1	Total Endosulfan	Not Set	0.0018	0.03	<0.00001
2	S1	Pirimiphos-methyl	Not Set	0.068	0.152	<0.00005
5	S1	Maldison	Not Set	0.032	0.151	<0.0005
7	S1	Maldison	Not Set	0.032	0.151	< 0.002
9	S1	Maldison	Not Set	0.032	0.151	<0.001
10	S1	Total Cypermethrin	Not Set	0.33	0.401	< 0.00005
11	S1	Maldison	Not Set	0.032	0.151	<0.00017
14	S1	Total Chlordane	0.00106	N/A	N/A	<0.0005
14	S1	p,p'-DDT	Not Set	0.0048	0.00824	<0.0020
15	S1	Maldison	Not Set	0.032	0.151	< 0.002
16	S1	Total Chlordane	0.00106	N/A	N/A	<0.0005
16	S1	p,p'-DDT	Not Set	0.0048	0.00824	<0.0020
17	S1	Maldison	Not Set	0.032	0.151	<0.001

*Robust average (assigned value not set).

6.6 Reporting of Additional Analytes

Additional analytes reported by participants are presented in Table 36.

In general, participants should take care to avoid any potential cross-contamination when analysing their samples.

Table 36 Additional Analytes Reported by Participants

Lab. Code	Sample	Analyte	Result (mg/L)	Uncertainty (mg/L)	Recovery (%)
10	S1	Fenthion	0.029	0.0087	NR
13	S2	Trichlopyr	0.0001	0.000028	NR
14	S1	Dimethoate	0.0005	0.0002	85.2

6.7 Fitness for Purpose of Results – Australian Drinking Water Guidelines

The Australian Drinking Water Guidelines (ADWG) provide a nationally recognised framework for assessing and managing drinking water quality to protect public health and ensure water is safe for consumption.[5] Accurate measurement of pesticides in potable water is essential, as analytical results must reliably indicate whether a water sample complies with the relevant guideline values.

The spiked values for analytes in this study, together with the corresponding ADWG guideline values, are presented in Table 1.

The ADWG specifies that comparison of results against the guideline value 'should occur at the level of one significant figure (s.f.)'.[5] The consequence is that any rounded value less than

or equal to the guideline value does not exceed the guideline, while any rounded value greater than the guideline value exceeds the guideline.[5]

More generally, when a test result is used to determine whether a sample complies with an upper control limit, the measurement uncertainty of that result is critical. ISO/IEC 17025 defines a decision rule for such assessments as a 'rule that describes how measurement uncertainty is accounted for when stating conformity with a specified requirement'.[8] To determine whether a sample meets a regulatory limit, considering the reported result and its associated uncertainty, decision rules generally provide three possible outcomes: Pass, Fail, or Inconclusive when further testing may be required (Figure 30).[10]

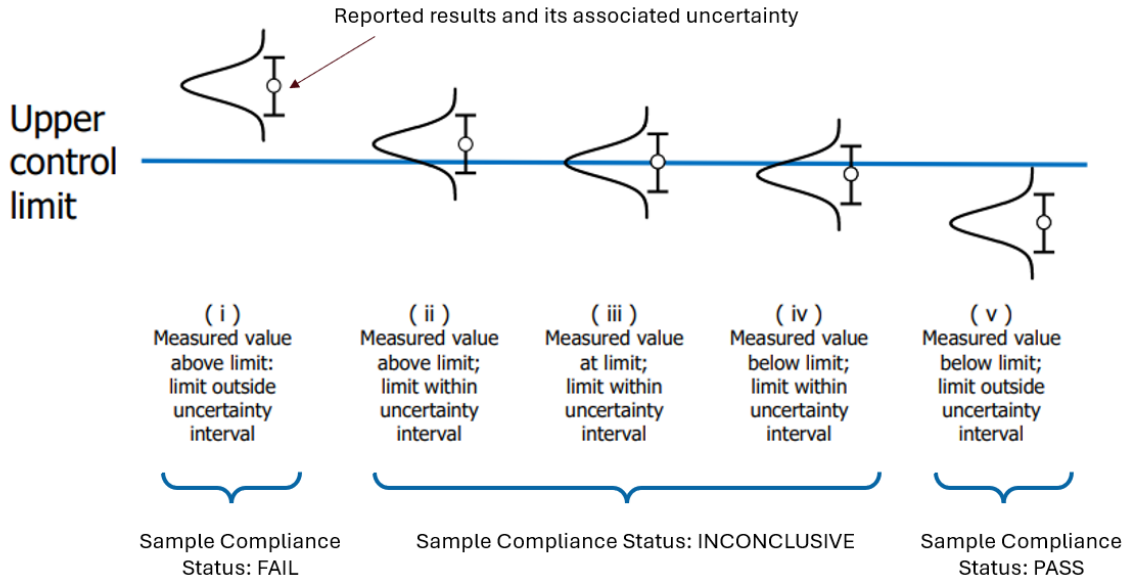


Image adapted from: Eurachem/CITAC Guide Use of Uncertainty Information in Compliance Assessment[10]

Figure 30 Assessment of Compliance with an Upper Limit

Figures 31 to 51 show comparisons of the actual (with uncertainty) and rounded spiked value (SV), assigned value (AV), and participants' results, as well as the guideline value (ADWG). Only numeric results have been included.

In this study, 11 scored analytes had spiked and assigned values that agreed on whether the sample complied with the relevant ADWG. The charts for these analytes are presented in Figures 31 to 41. For these analytes, of the 113 results assessed against the Australian Drinking Water Guidelines, 102 (90%) correctly reflected whether the sample exceeded the guideline or not.

In most cases, participants who returned the incorrect compliance status had a significant positive or negative bias in their reported result. These participants should review their methodology to identify the source of this bias.

Some results had uncertainties spanning the guideline value. This may have resulted in an inconclusive compliance assessment, leading to unnecessary further testing. In some cases, this was due to the analyte being close in concentration to the ADWG, so even participants with reasonable uncertainty evaluations had uncertainties spanning the guideline value. However, for analytes where the level present was significantly different to the ADWG, participants with uncertainties spanning the guideline value should review their uncertainty evaluations to ensure that these are not too large to be fit-for-purpose.

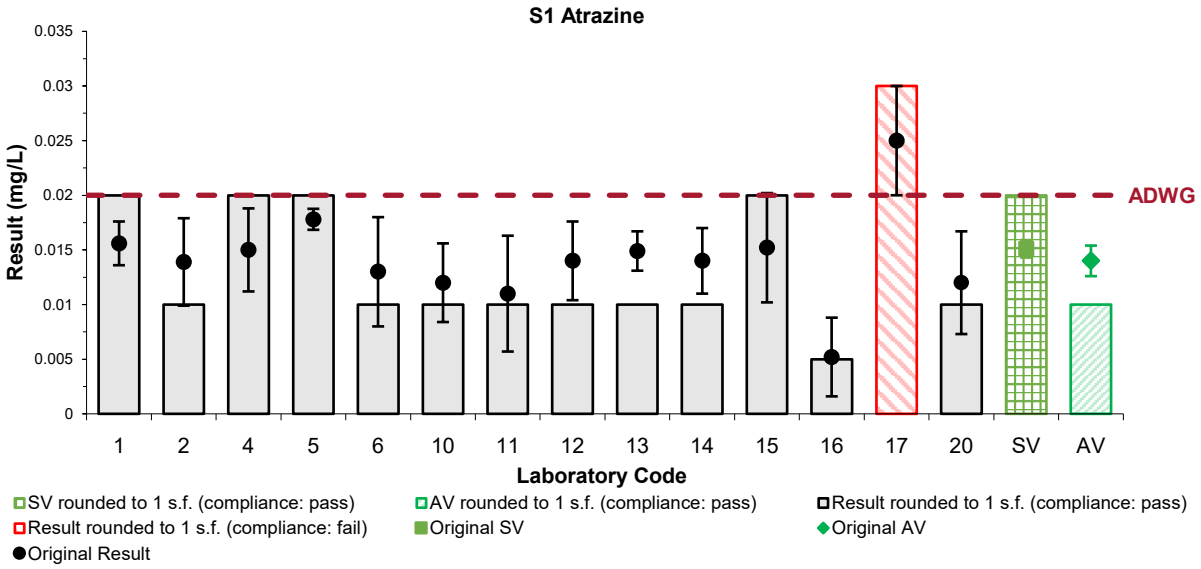


Figure 31 Sample S1 Atrazine Results and Guideline Value

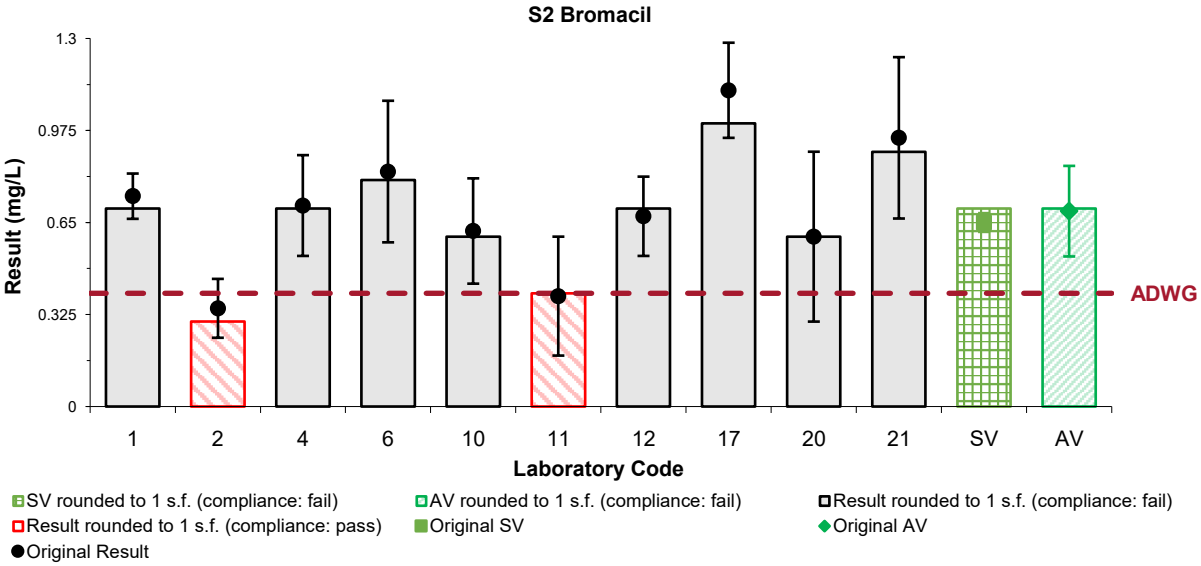


Figure 32 Sample S2 Bromacil Results and Guideline Value

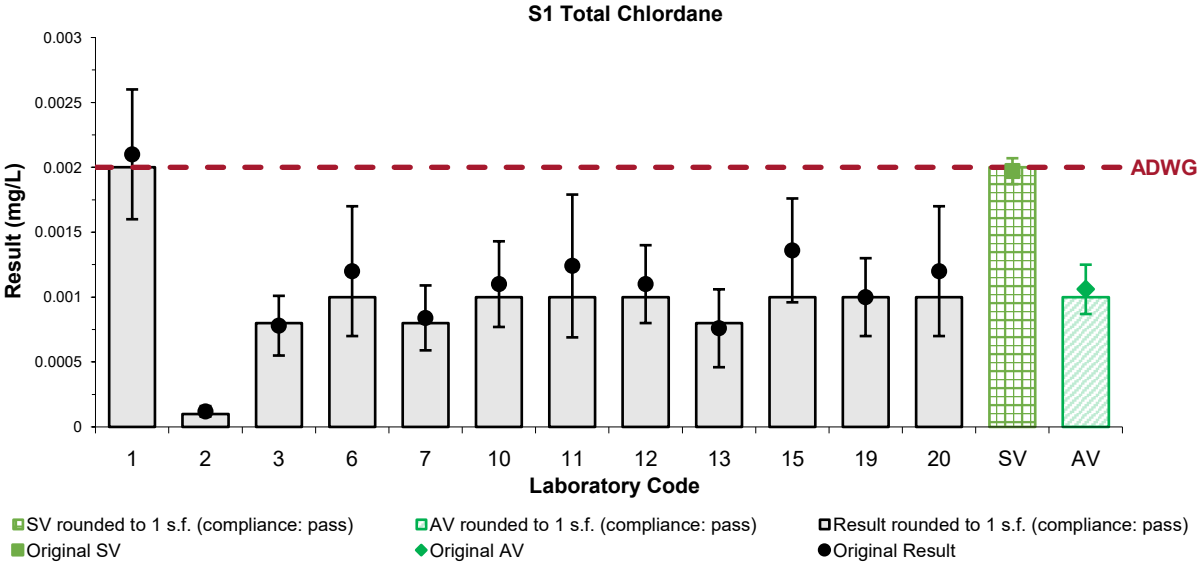


Figure 33 Sample S1 Total Chlordane Results and Guideline Value

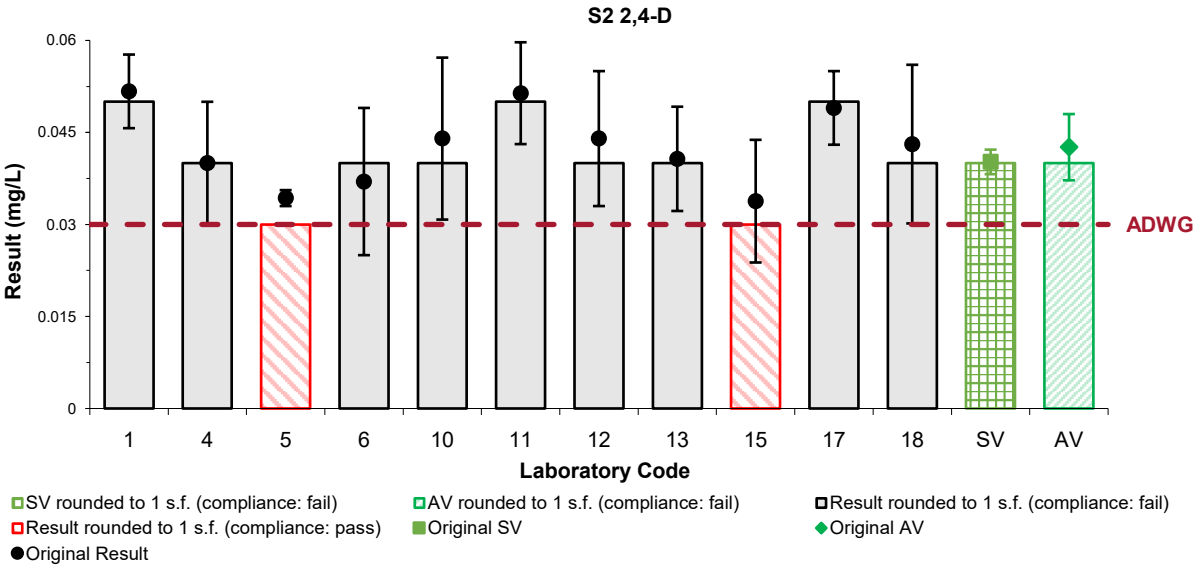


Figure 34 Sample S2 2,4-D Results and Guideline Value

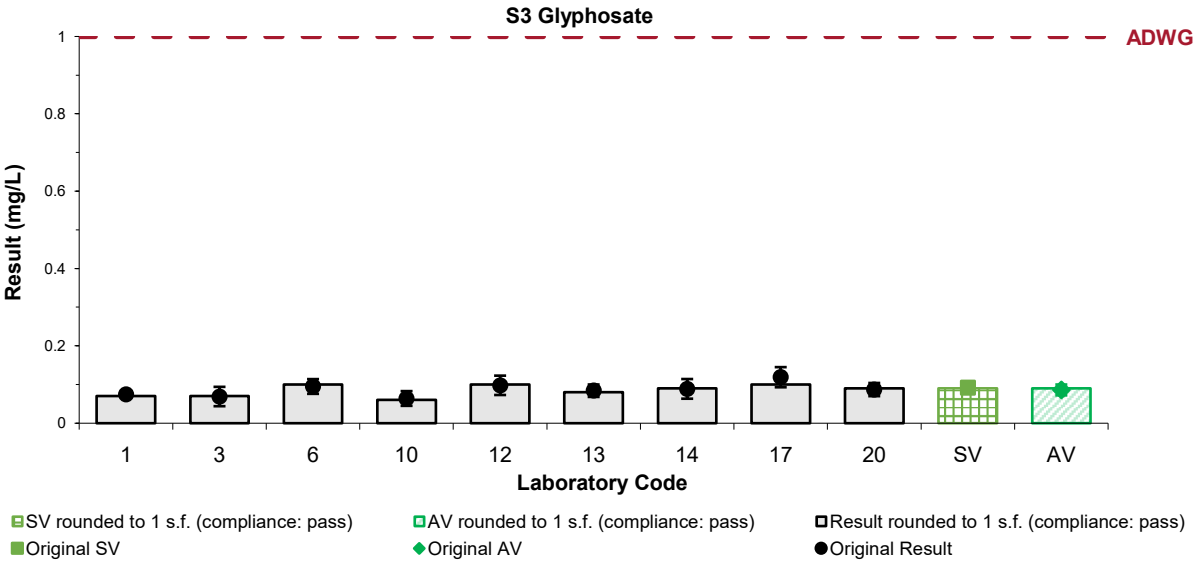


Figure 35 Sample S3 Glyphosate Results and Guideline Value

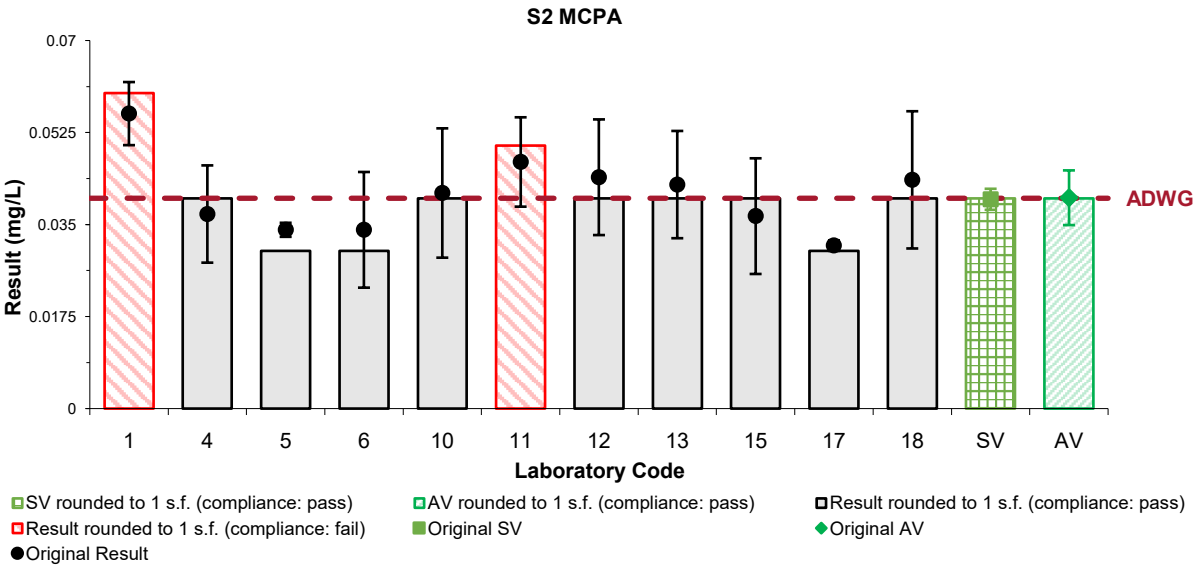
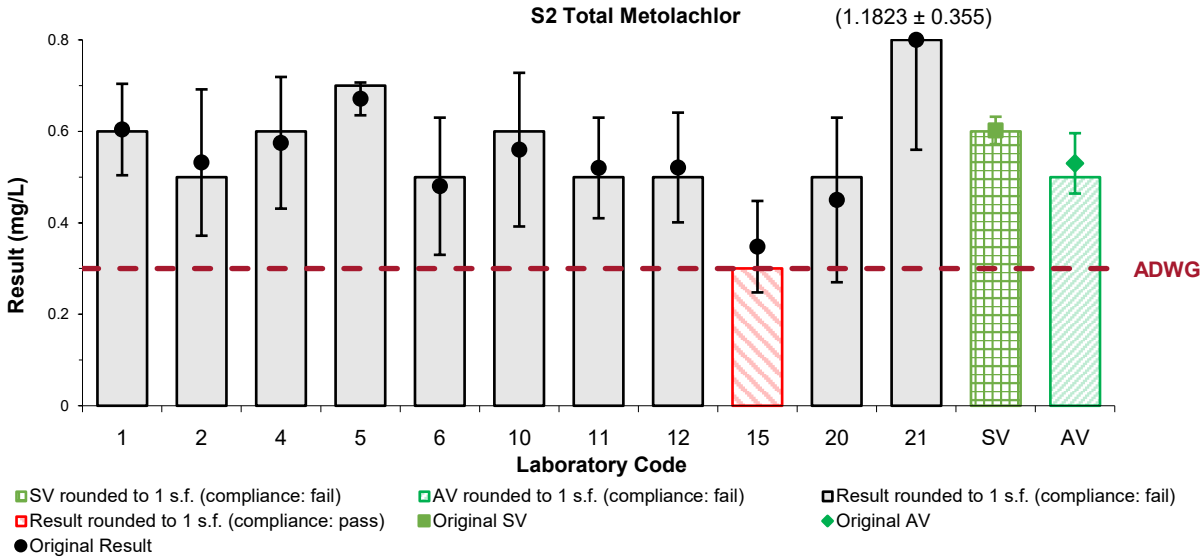


Figure 36 Sample S2 MCPA Results and Guideline Value



Result from Laboratory 21 has been scaled to fit the chart; original result in parentheses.

Figure 37 Sample S2 Total Metolachlor Results and Guideline Value

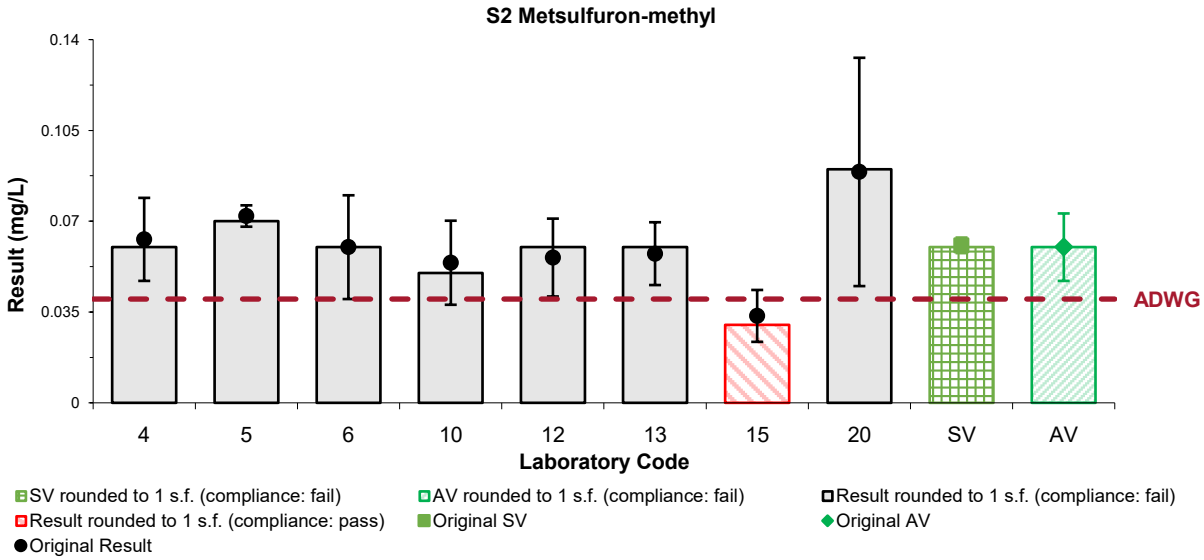


Figure 38 Sample S2 Metsulfuron-methyl Results and Guideline Value

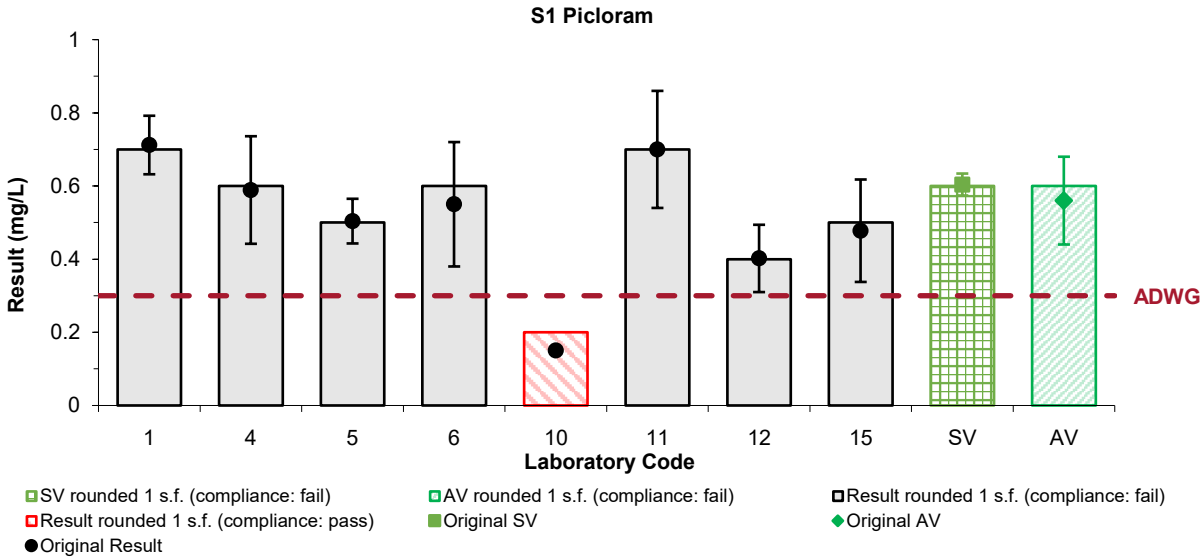


Figure 39 Sample S1 Picloram Results and Guideline Value

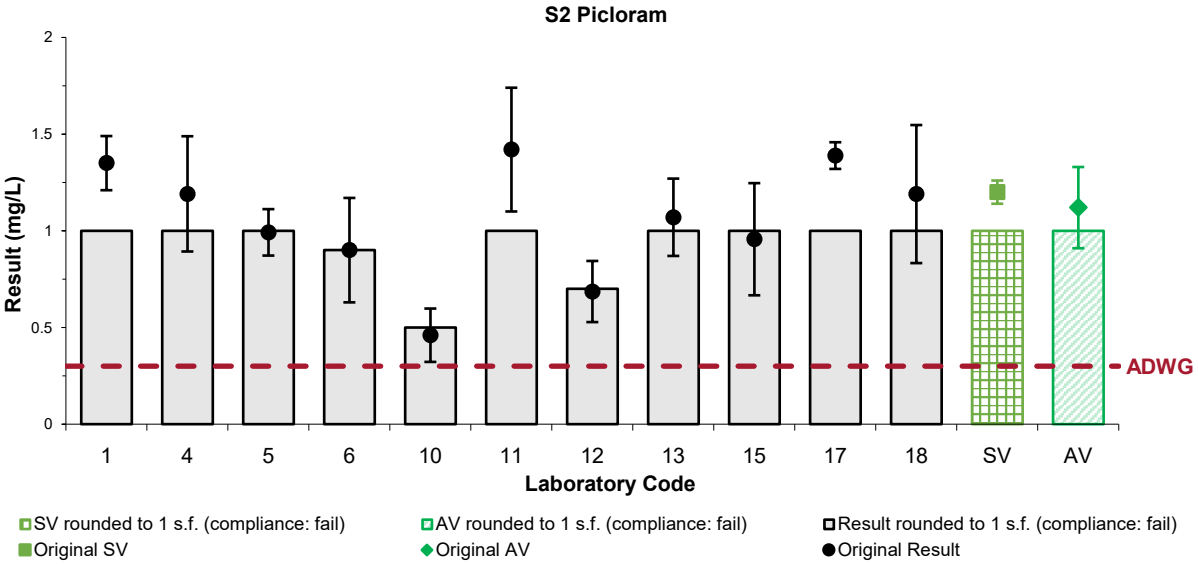


Figure 40 Sample S2 Picloram Results and Guideline Value

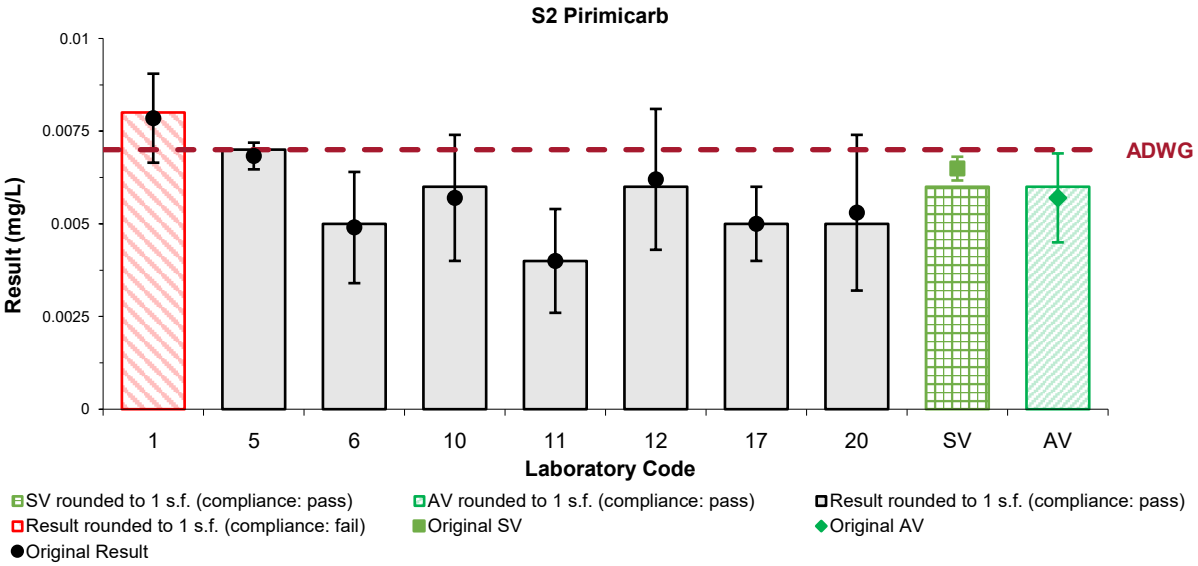


Figure 41 Sample S2 Pirimicarb Results and Guideline Value

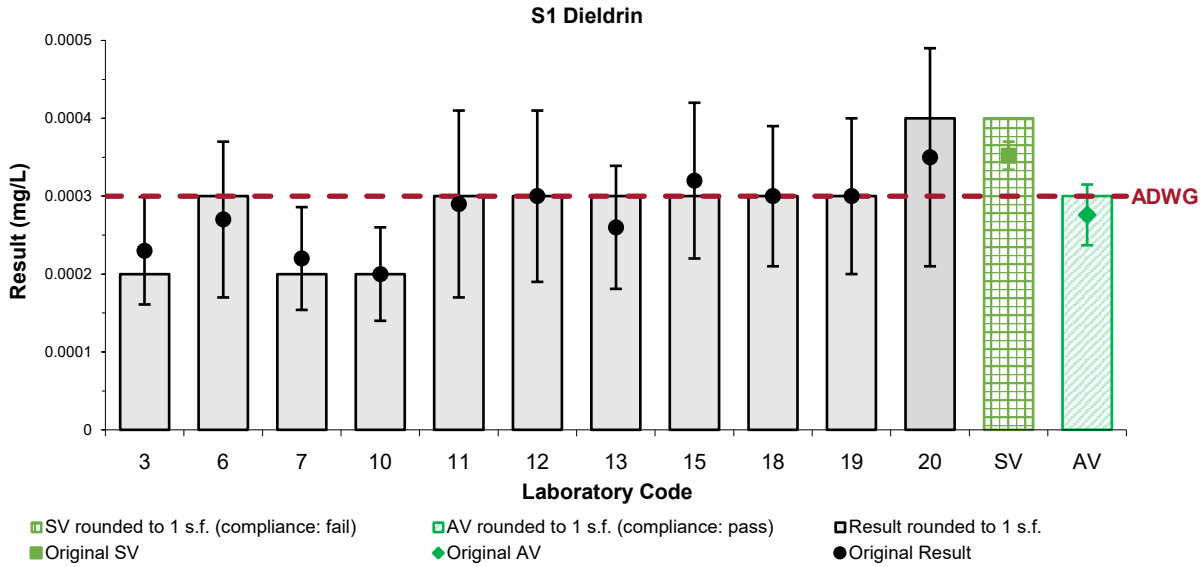
Sample S1 was prepared with both dieldrin and total propiconazole concentrations exceeding the ADWG. For both analytes, the results reported by participants exhibited a negative bias, resulting in assigned values lower than the spiked values.

For dieldrin, both the original and rounded assigned values indicated compliance with the ADWG. However, the uncertainty associated with the assigned value spanned the guideline.

For total propiconazole, the original assigned value remained above the ADWG, inclusive of uncertainty. However, after rounding to one significant figure, it indicated compliance instead.

The true cause of the bias in the assigned value as compared to the spiked value is unknown. Assessing laboratory compliance with the ADWG is challenging when values are required to be rounded to one significant figure, and analytes are present at levels close to the guideline.

Therefore, compliance assessment was not performed for these two analytes, and their plots are presented for information only in Figures 42 and 43.



The ADWG value is for aldrin and dieldrin combined. Sample S1 was spiked with dieldrin only.

Figure 42 Sample S1 Dieldrin Results and Guideline Value

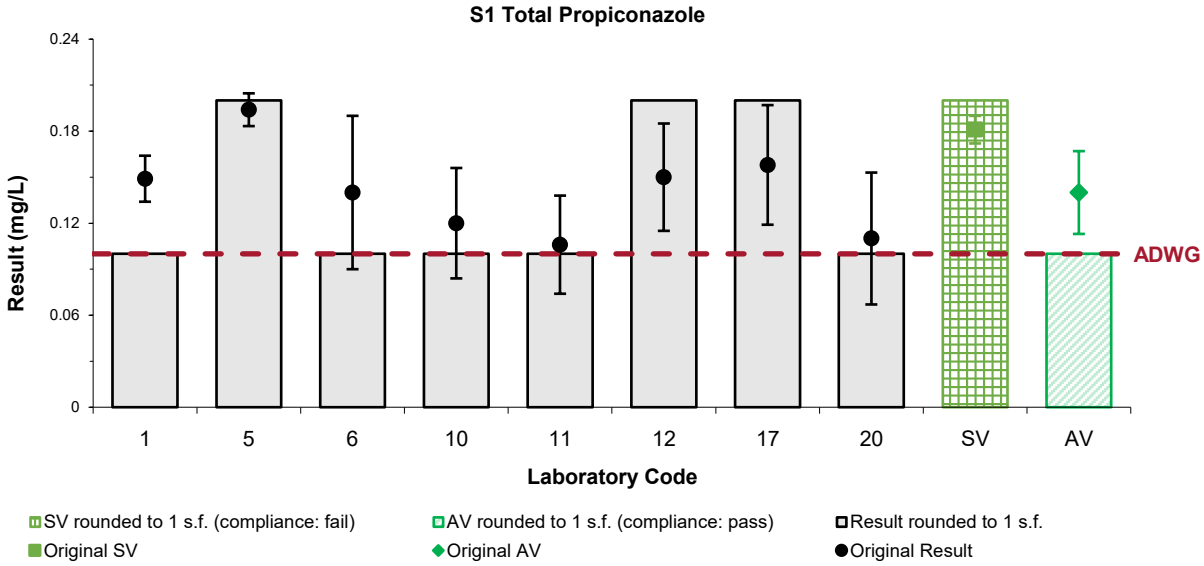


Figure 43 Sample S1 Total Propiconazole Results and Guideline Value

For the analytes with no assigned values, the results and guideline values are presented in Figures 44 to 51 for information only.

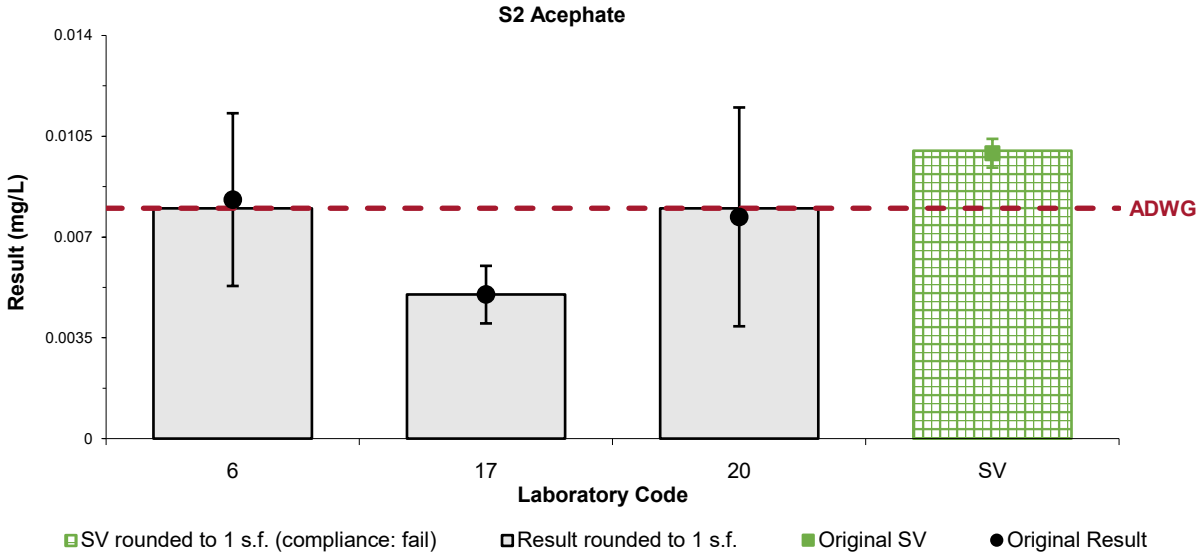


Figure 44 Sample S2 Acephate Results and Guideline Value

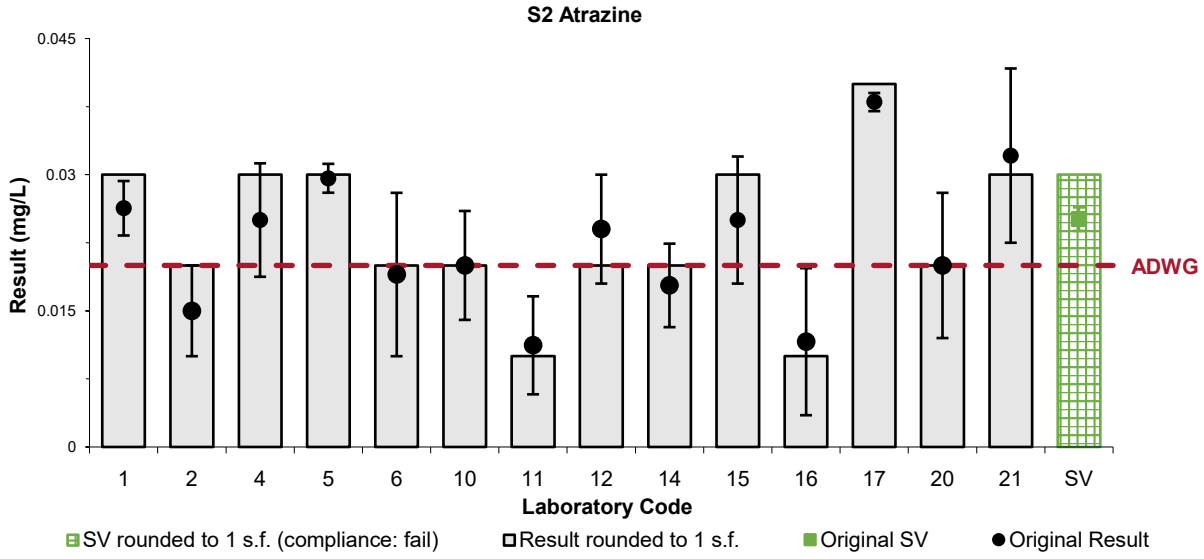
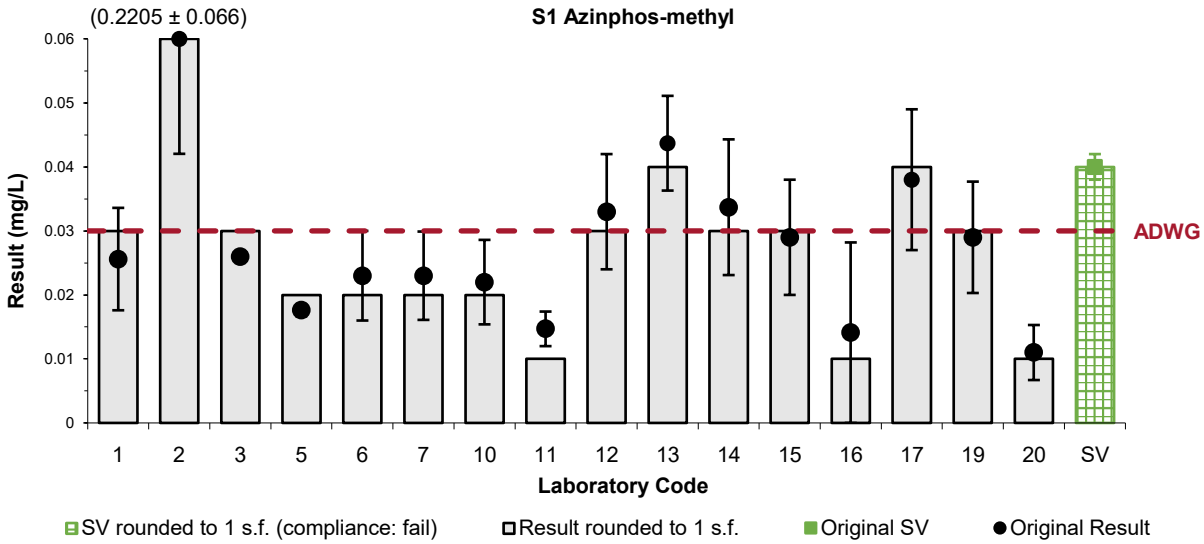


Figure 45 Sample S2 Atrazine Results and Guideline Value



Result from Laboratory 2 has been scaled to fit the chart; original result in parentheses.

Figure 46 Sample S1 Azinphos-methyl Results and Guideline Value

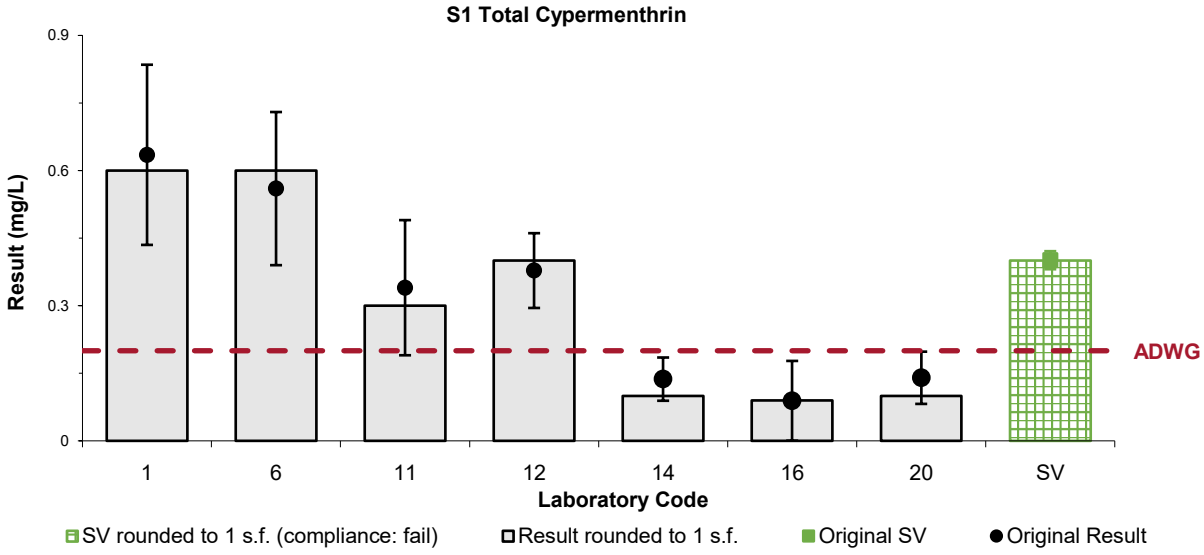


Figure 47 Sample S1 Total Cypermethrin Results and Guideline Value

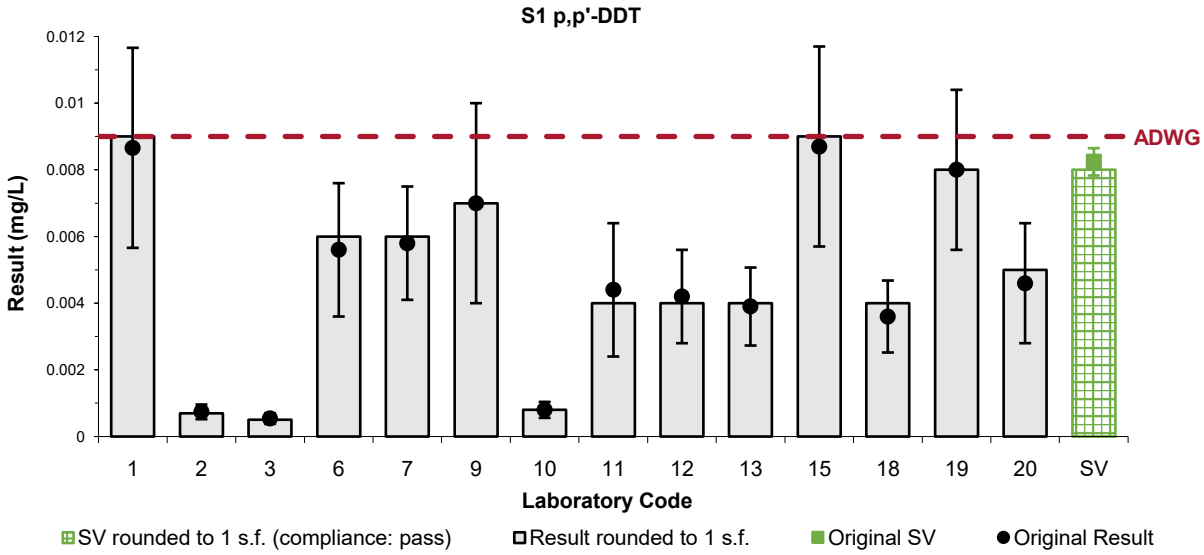


Figure 48 Sample S1 p,p'-DDT Results and Guideline Value

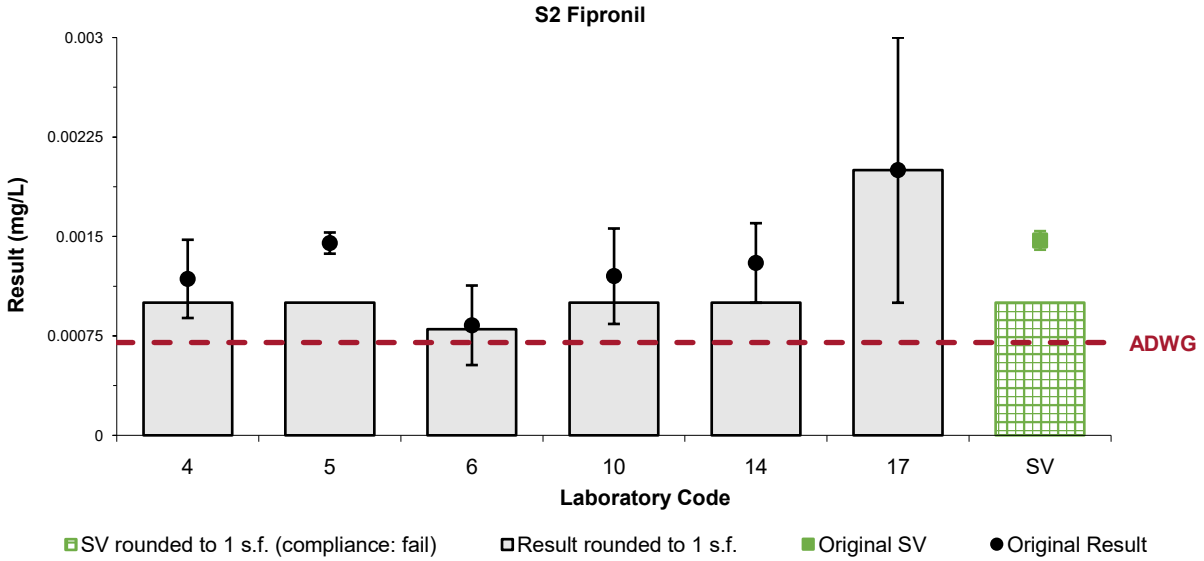


Figure 49 Sample S2 Fipronil Results and Guideline Value

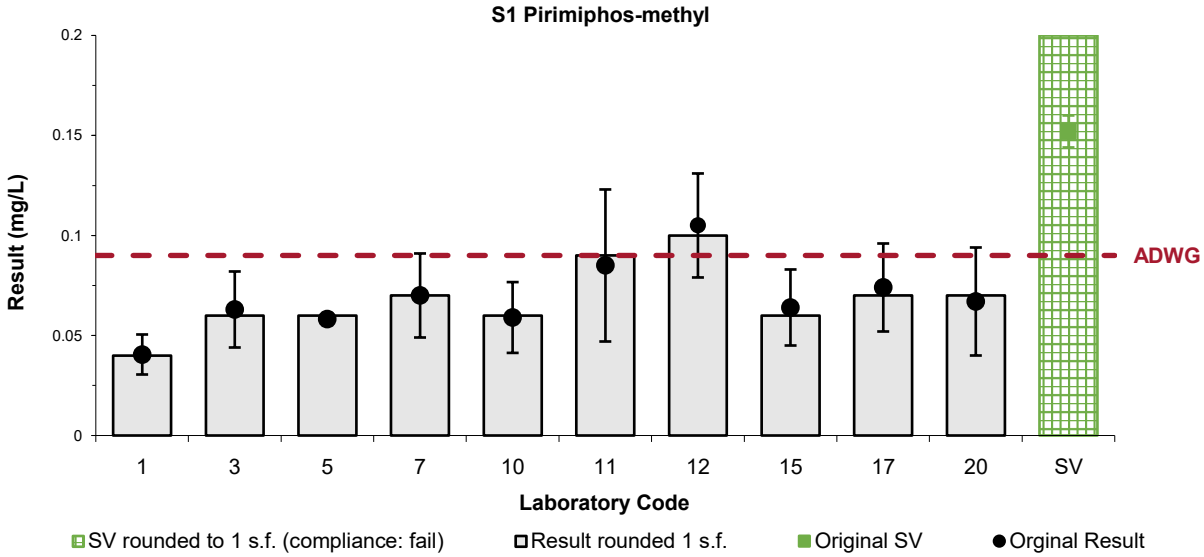


Figure 50 Sample S1 Pirimiphos-methyl Results and Guideline Value

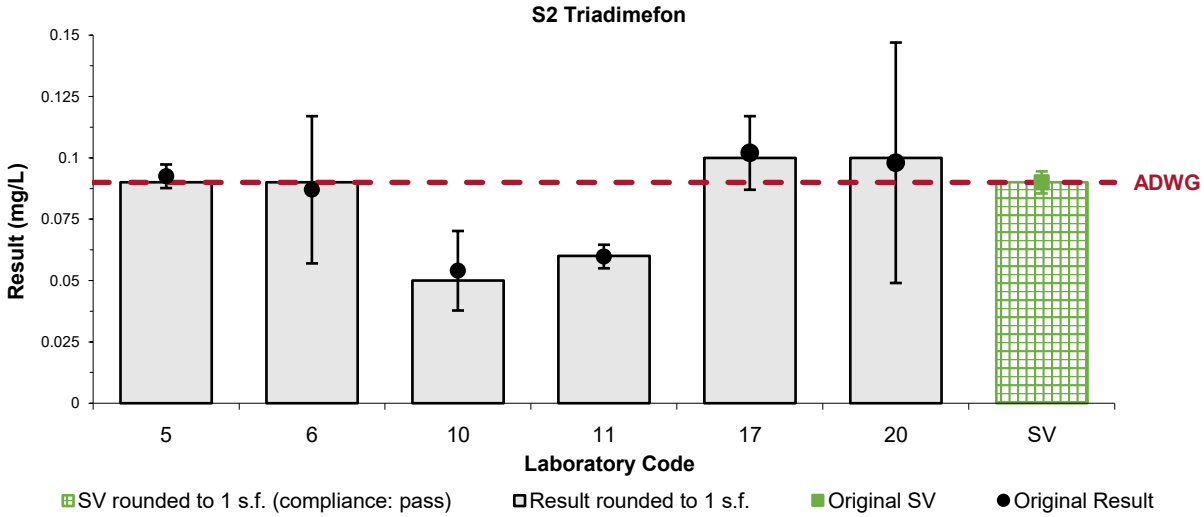


Figure 51 Sample S2 Triadimefon Results and Guideline Value

Significant instability was observed for Sample S1 total endosulfan and maldison (discussed further in Section 6.8). The spiked values should be interpreted with caution, as they may not accurately represent the actual sample conditions at the time of analysis. Consequently, these analytes have been excluded from this section, and no assessment of sample compliance has been made.

6.8 Participants' Analytical Methods

Results excluded from Section 5 have also been excluded in this section, so as to not bias the discussion of the analytical methods used.

Participants used a variety of analytical methods for the test samples (Appendix 4).

For Samples S1 and S2, participants could choose either 1 x 500 mL bottle or 3 x 100 mL bottles, depending on which option best suited their laboratory's method. Participants reported test portions ranging from 1 mL to the entire bottle, with some participants reporting that they also rinsed the bottle. For Sample S3 (AMPA and glyphosate), participants were provided with a 500 mL bottle. All participants used less than 10 mL for this analysis. A comparison of *z*-scores and sample volume used for scored analytes is presented in Figures 52 and 53. No evident correlation was observed for using different volumes.

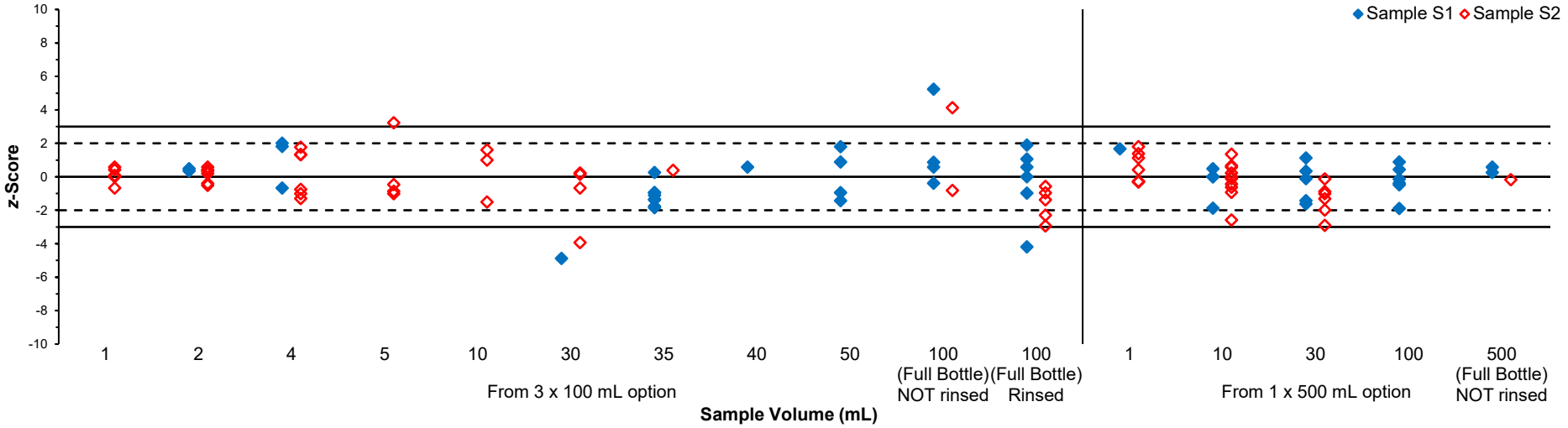


Figure 52 Samples S1 and S2 z-Score vs Sample Volume

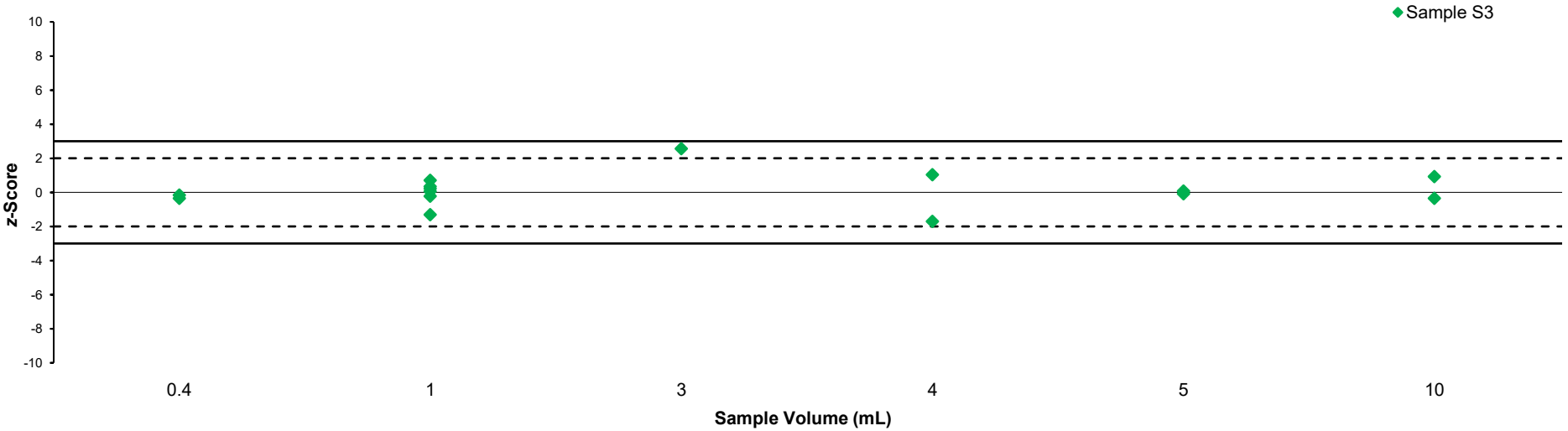


Figure 53 Sample S3 z-Score vs Sample Volume

The sample extraction and preparation techniques reported by participants included:

- Dilution;
- Derivatisation;
- Hydrolysis;
- Liquid-liquid extraction (LLE);
- Solid-phase extraction (SPE); and
- Direct injection (DI).

Where participants did not use direct injection, the following extraction solvents were listed:

- Dichloromethane (DCM);
- Acetonitrile (ACN);
- Methanol (MeOH);
- Diethyl ether;
- Methyl tert-butyl ether (MTBE);
- Ethyl acetate (EtOAc);
- Hexane (Hex);
- Acetone (Ace); or
- Combinations of the above solvents.

Instrumental techniques used by participants included:

- Gas chromatography (GC) coupled to mass spectrometry (MS), tandem mass spectrometry (MS/MS), or electron capture detection (ECD); or
- Liquid chromatography (LC) coupled to MS(/MS), diode array detection (DAD), or fluorescence detection (FLD).

The most common method used was LLE with DCM, and using GC-MS(/MS) for analysis.

Individual Analyte Commentary

Total Chlordane Sample S1 was spiked with both cis-chlordane and trans-chlordane in a 1:1 ratio, with participants requested to report for total chlordane. Out of 12 results, 11 returned acceptable z-scores. Laboratory 2 reported a result that was approximately 9 times lower than the assigned value. This participant may need to check if they have made a reporting error (for example, decimal point error), or a dilution calculation error.

p,p'-DDT challenged participants, and there was no agreement between results (Figure 54). There was also poor recovery of the spiked analyte; this has been observed in previous NMIA water PT studies.

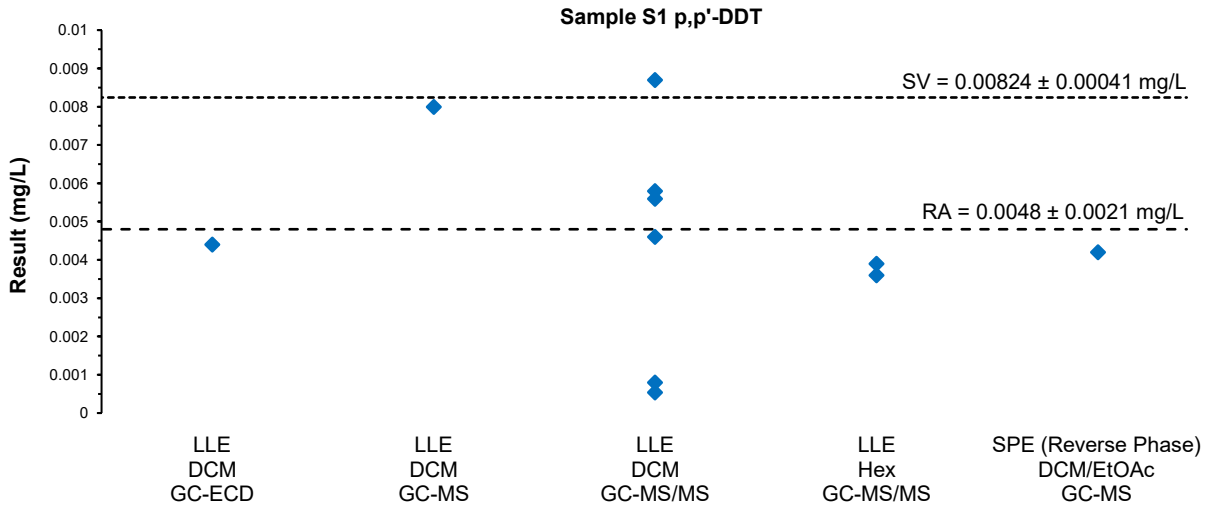


Figure 54 Sample S1 p,p'-DDT Result vs Methodology

Dieldrin Participants performed well, with all achieving an acceptable result.

Endosulfan Significant instability was observed for this analyte, resulting in poor recovery of the spiked analyte and very variable results reported. Endosulfan has been shown to degrade in water. Breakdown products include endosulfan sulfate and endosulfan diol.[11] In general, participants were asked to only report the named analyte in the results sheet. This ensures consistency in the results reported, as different guidelines internationally may refer to different combinations of analytes. For example, the ADWG specifies for endosulfan that 'the sum of the α- and β-isomers plus the endosulfan sulfate metabolite … have to be considered'.[5] In future PT studies, key metabolites and breakdown products will also be requested separately on the results sheet.

Acephate Only 3 participants tested for this analyte. Participants using direct injection achieved better recovery of the spiked analyte (Figure 55).

Azinphos-methyl This was the first NMIA PT study with this analyte in water. This analyte challenged participants. A wide variety of methodologies were used, and these did not produce compatible results (Figure 56).

Maldison had significant instability. This analyte has a short half-life in aqueous environments, particularly in alkaline conditions.[12] As for endosulfan, future PT studies will have key metabolites and breakdown products requested separately on the results sheet.

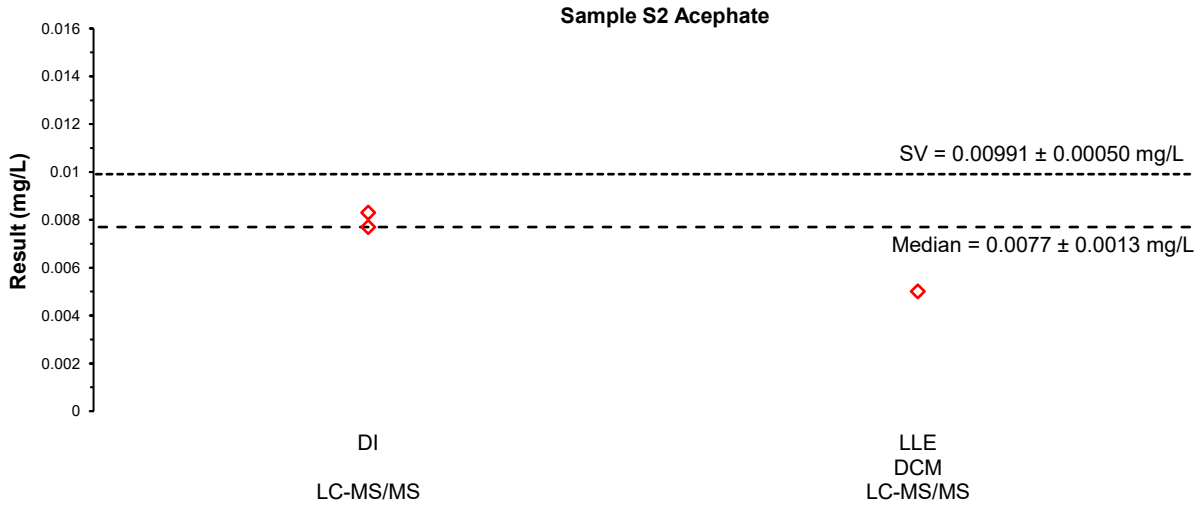


Figure 55 Sample S2 Acephate Result vs Methodology

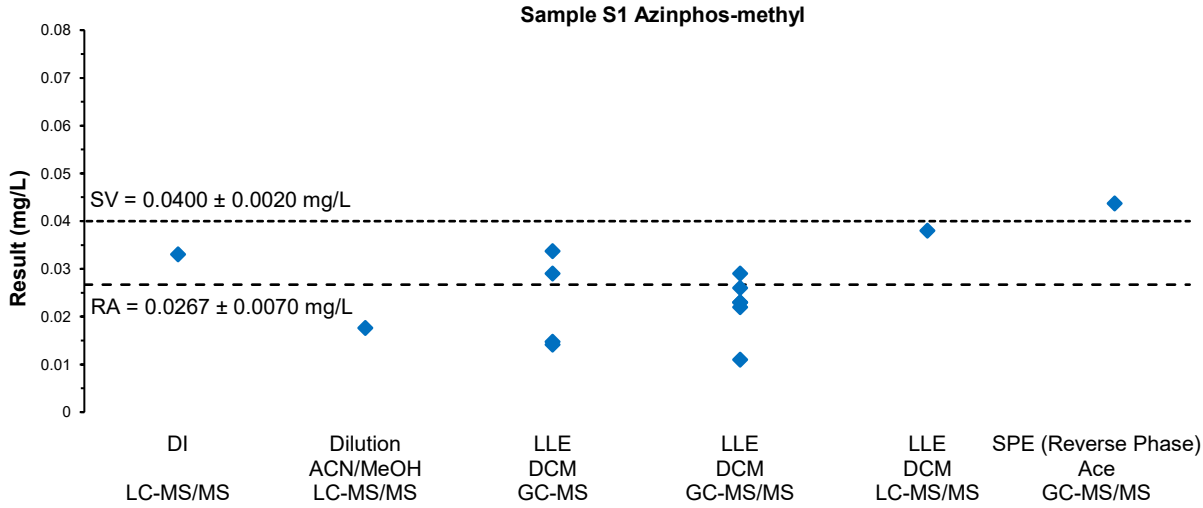


Figure 56 Sample S1 Azinphos-methyl Result vs Methodology

Pirimiphos-methyl was spiked for the first time in a NMIA PT study in water. Participants used either LLE with DCM followed by GC-MS(/MS) for analysis, or dilution or direct injection into LC. There was consistent low recovery of the spiked analyte regardless of methodology used.

2,4-D and **MCPA** Participants performed well for both analytes, with excellent agreement between most of the results and the spiked value. Twenty-one out of 22 results returned acceptable z-scores. The most common method used was DI into LC-MS/MS.

Picloram was spiked into both Samples S1 and S2. Participants used a variety of methods, and most produced compatible results (Figure 57). One participant performed a diazomethane derivatisation and returned results biased low in both samples. This participant may need to review their procedure to ensure that the derivatisation goes to completion, as an incomplete reaction may be contributing to the negative bias of their picloram results.

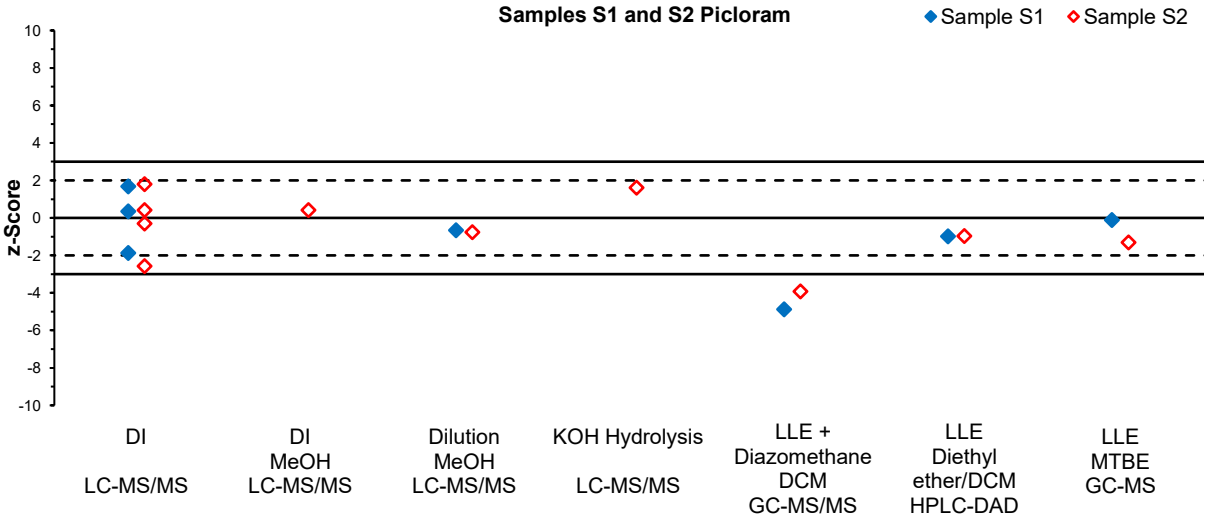


Figure 57 Samples S1 and S2 Picloram z-Score vs Methodology

Atrazine was spiked into both Samples S1 and S2, with Sample S2 being spiked at a higher level. There was good agreement between results for Sample S1, and an assigned value could be set. However, no assigned value could be set for Sample S2 due to the higher variability observed.

A variety of methodologies were employed in this study (Figure 58). Participants were requested to report whether they used any internal standards for the correction of instrument variation. In this study, participants using isotopically labelled analogues as internal standards returned results close to the spiked concentration of atrazine in both samples, whereas there was a greater spread of results returned by the other participants (Figure 59).

Bromacil Most participants were not challenged by this analyte. Results from participants who used DI into the LC-MS/MS, or SPE followed by GC-MS, performed acceptably (Figure 60).

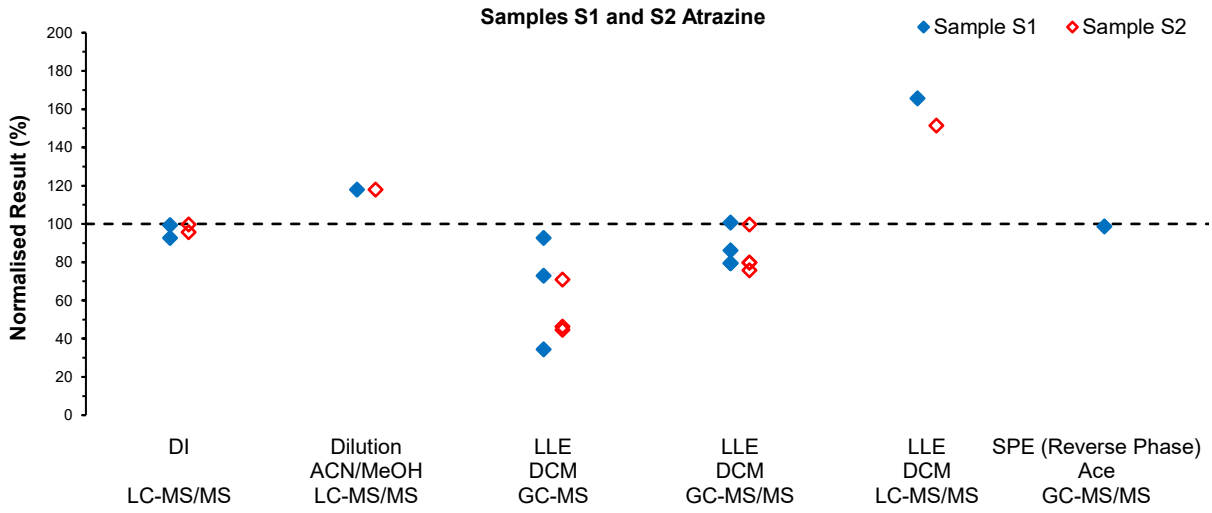


Figure 58 Samples S1 and S2 Atrazine Result Normalised to Spiked Value vs Methodology

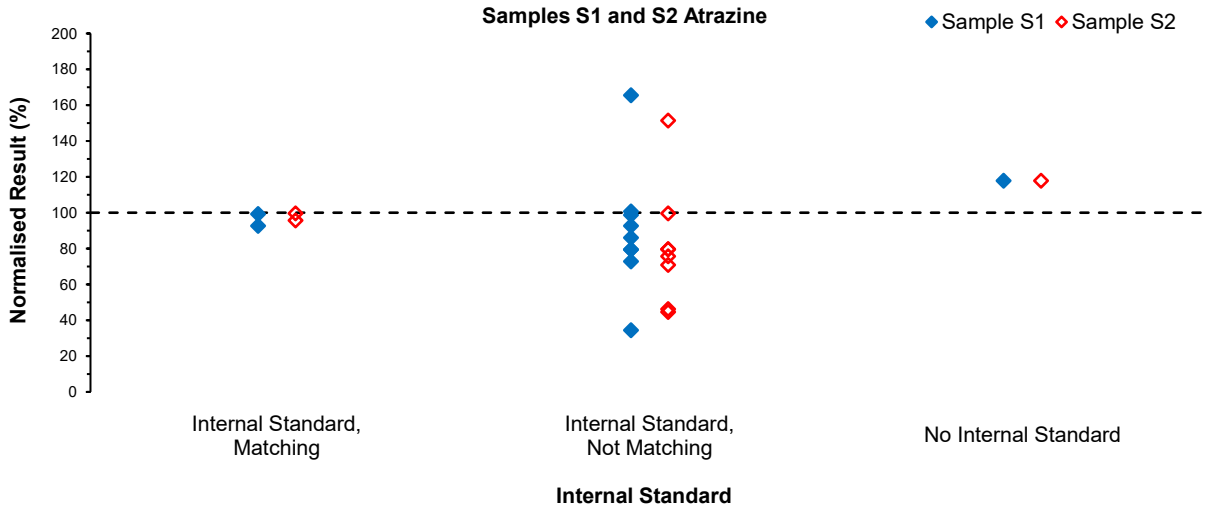


Figure 59 Samples S1 and S2 Atrazine Result Normalised to Spiked Value vs Internal Standard

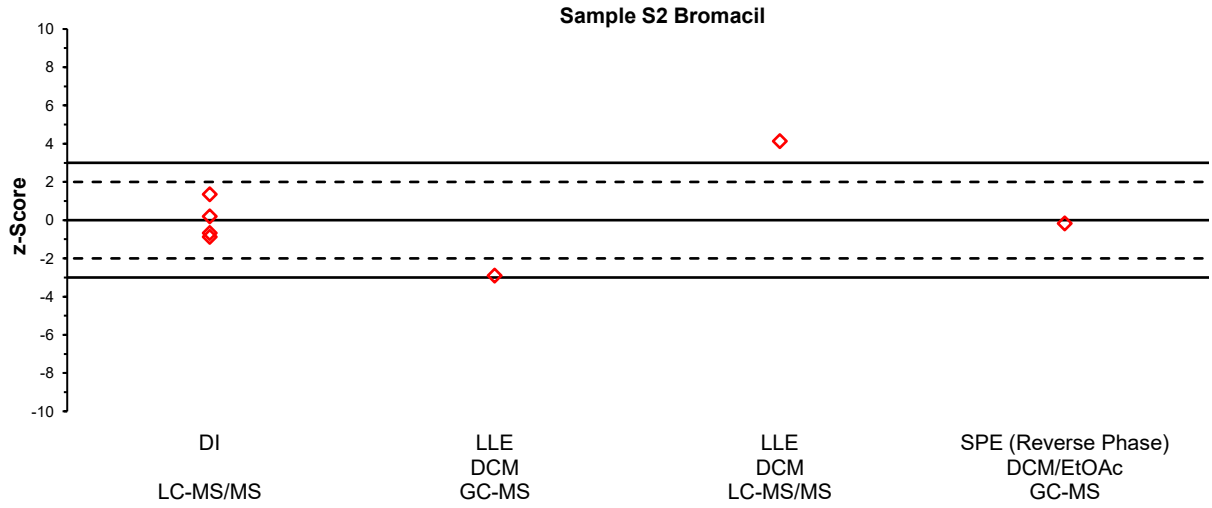


Figure 60 Sample S2 Bromacil Result vs Methodology

Total Cypermethrin This usually is found as a mixture of various isomers, however in this study only the α-cypermethrin isomers were added to the sample. An assigned value could not be set for this analyte due to the variability of results. Plots of results versus methodology parameters are presented in Figures 61 to 63. Longer extraction times may allow for more effective extraction of this analyte from the matrix. On the other hand, higher temperatures used for extract concentration may cause analyte degradation, particularly if water is still present in the extract.[13]

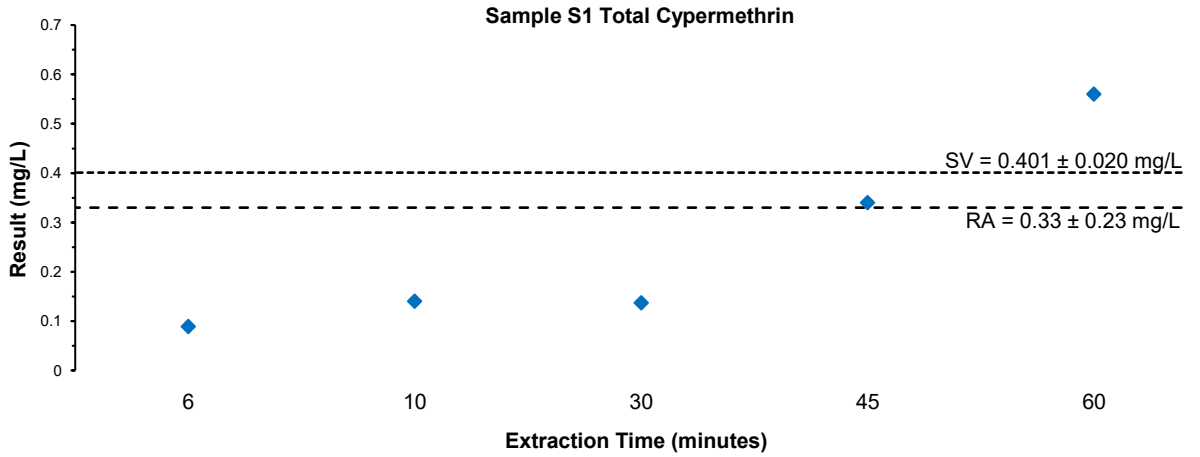


Figure 61 Sample S1 Total Cypermethrin Result vs Extraction Time

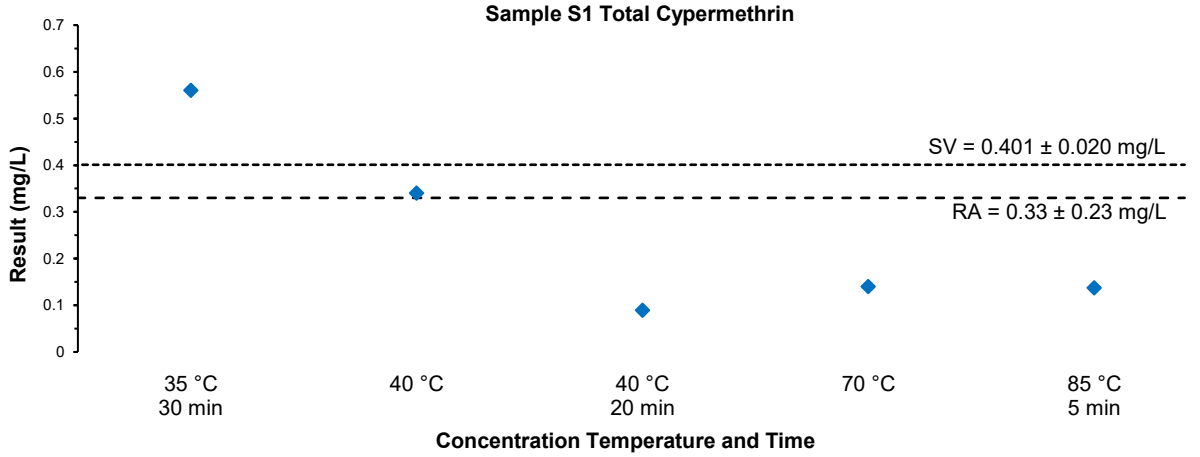


Figure 62 Sample S1 Total Cypermethrin Result vs Extract Concentration Temperature and Time

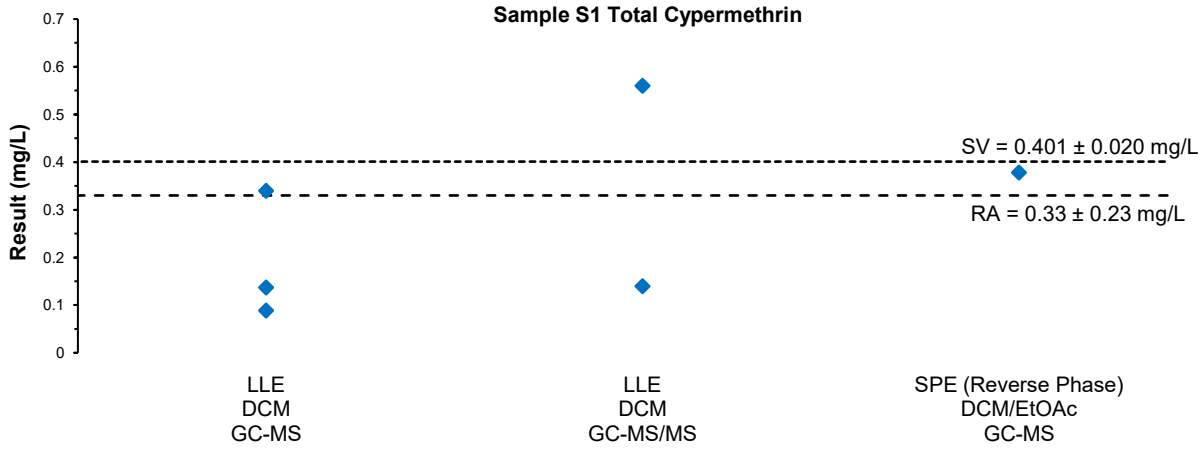


Figure 63 Sample S1 Total Cypermethrin Result vs Methodology

Fipronil Five of the 6 reported results were in good agreement with each other.

Total Metolachlor Out of 11 results, 10 returned acceptable z-scores. Laboratory 21 reported a result that was approximately 2 times higher than the assigned value. This participant may need to check their standard or dilution preparation and calculation procedure.

Metsulfuron-methyl For most participants this was not a challenging analyte, with 6 out of 8 results being in excellent agreement with each other and the spiked value (Figure 64).

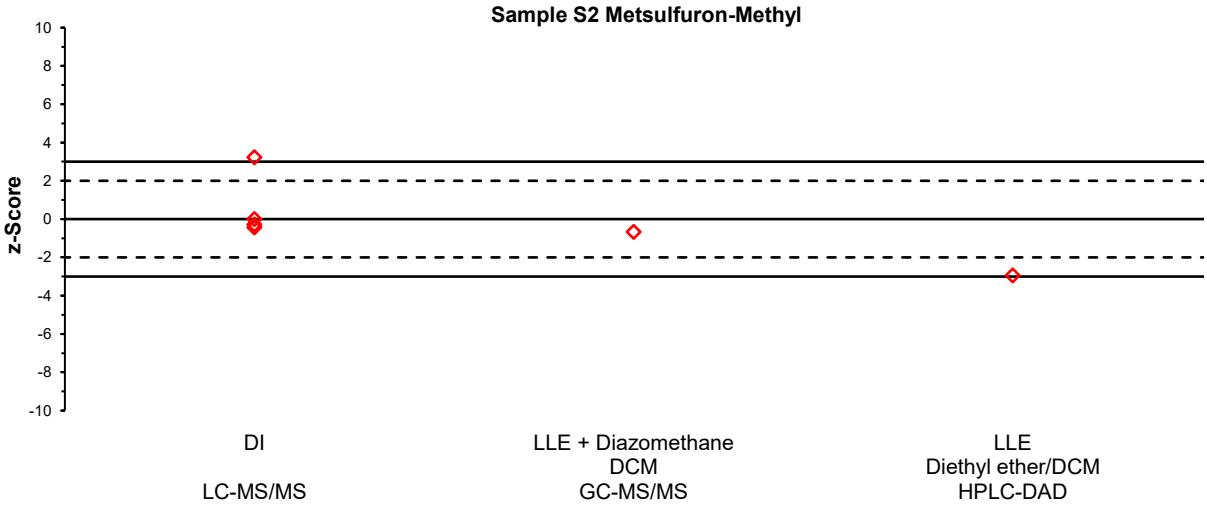


Figure 64 Sample S2 Metsulfuron-methyl z-Score vs Methodology

Pirimicarb Seven out of 8 results returned acceptable z-scores. Both GC and LC analytical techniques were used, and these generally produced compatible results.

Propazine was present in Sample S2 at a low level. Four participants reported results for this analyte, and all results were in excellent agreement with each other.

Total Propiconazole All 8 participants reporting numeric results for this analyte performed acceptably. Both GC and LC analytical techniques were used, and these produced compatible results.

Triadimefon Four of the 6 results reported were in good agreement with each other and the spiked value. In this study, participants using GC-MS(/MS) for analysis returned results that were biased low (Figure 65).

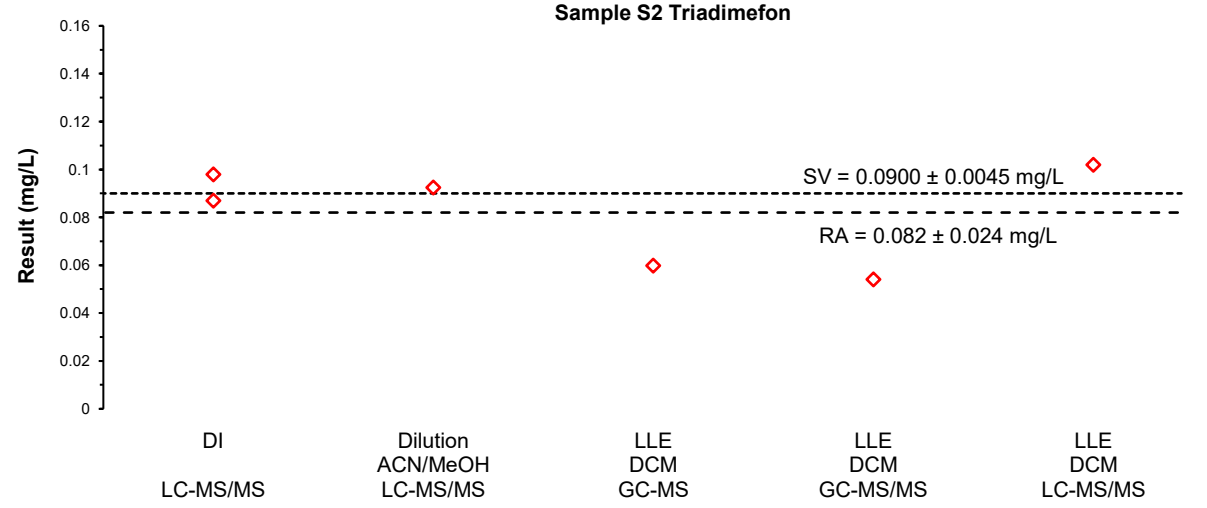


Figure 65 Sample S2 Triadimefon Result vs Methodology

Glyphosate and **AMPA** These highly polar analytes did not challenge participants, with 15 of the 16 results across the two analytes returning an acceptable z-score. Most participants performed derivatisation (for example, with 9-fluorenylmethoxycarbonyl (FMOC)) and direct injection. All participants used either LC-MS(/MS) or LC-FLD for analysis.

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. The recoveries reported were in the range of 54% to 129%. No participant reported that they corrected their results for recoveries.

6.9 Certified Reference Materials

Participants were requested to indicate whether certified standards or matrix reference materials had been used as part of the quality assurance for their analysis.

Fourteen participants reported using certified standards. The following were listed:

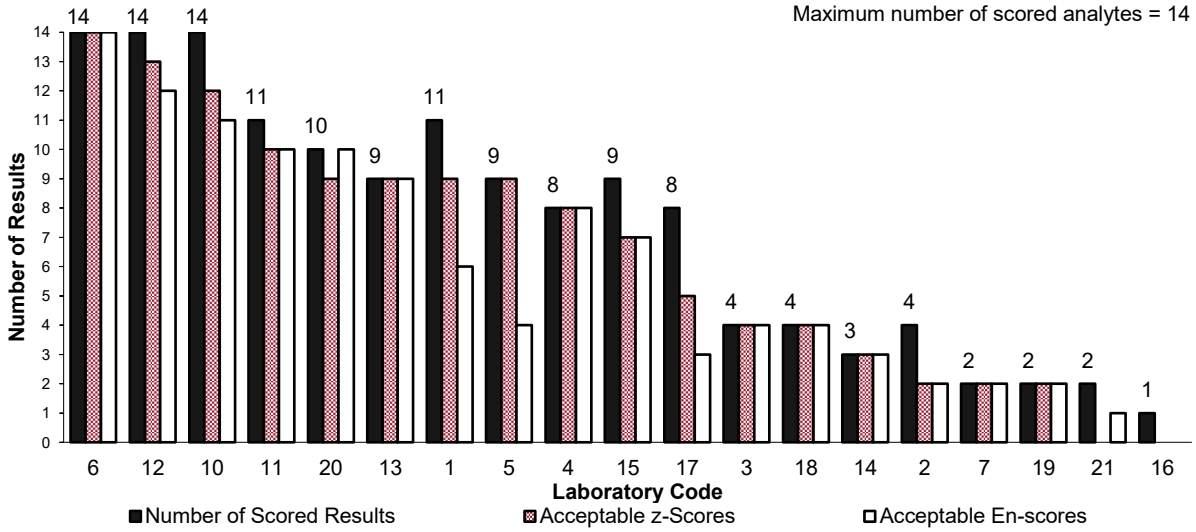
- Accustandard
- o2si
- PM Separations
- Certified reference materials
- ISO 17034 compliant standards
- LGC – Sigma

These materials may or may not meet the internationally recognised definition of a certified reference material:

> '***reference material**, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures*'[14]

6.10 Summary of Participants' Results and Performances

Summaries of participants' results and performances in this PT study are presented in Tables 37 to 39, and Figure 66.



Laboratories 7, 15, 18, and 19 analysed Samples S1 and S2 only (maximum of 12 scored analytes). Laboratory 9 did not report any scored results.

Figure 66 Summary of Participants' Performance

Table 37 Summary of Participants' Results and Performance for Sample S1*

Lab. Code	Atrazine	Azinphos-methyl	Total Chlordane	Total Cypermethrin	p,p'-DDT	Dieldrin	Total Endosulfan	Maldison	Picloram	Pirimiphos-methyl	Total Propiconazole
AV	0.0140	Not Set	0.00106	Not Set	Not Set	0.000276	Not Set	Not Set	0.56	Not Set	0.140
1	0.0156	0.0256	0.0021	0.635	0.00866	<0.0005	<0.005	0.0000588	0.712	0.0405	0.149
2	0.0139	0.2205	0.00012	NT	0.00074	<0.00005	<0.00001	0.045	NT	<0.00005	NT
3	NT	0.026	0.00078	NT	0.00054	0.00023	<0.0004	0.021	NT	0.063	NT
4	0.015	NT	NT	NT	NT	NT	NT	NT	0.589	NT	NT
5	0.0178	0.0176	NT	NT	NT	NT	NT	<0.0005	0.504	0.0582	0.194
6	0.013	0.023	0.0012	0.56	0.0056	0.00027	0.00029	0.00011	0.55	NT	0.14
7	NT	0.023	0.00084	NT	0.0058	0.00022	0.00023	< 0.002	NT	0.07	NT
9	NT	NT	NT	NT	0.007	<0.001	NT	<0.001	NT	NT	NT
10	0.012	0.022	0.0011	< 0.00005	0.0008	0.00020	0.0002	0.0710	0.15	0.059	0.12
11	0.011	0.0147	0.00124	0.34	0.0044	0.00029	0.00027	<0.00017	0.7	0.085	0.106
12	0.014	0.033	0.0011	0.378	0.0042	0.0003	0.0049	0.039	0.402	0.105	0.15
13	0.0149	0.0437	0.00076	NT	0.00390	0.00026	0.00869	0.0452	NT	NT	NT
14	0.014	0.0337	<0.0005	0.137	<0.0020	<0.0005	0.0016	0.0039	NT	NT	NT
15	0.0152	0.029	0.00136	< 0.2	0.0087	0.00032	0.00022	< 0.002	0.4777	0.064	NT
16	0.0052	0.0141	<0.0005	0.0889	<0.0020	<0.0005	0.0031	0.0176	NT	NT	NT
17	0.025	0.038	<0.002	NT	<0.01	<0.001	<0.002	<0.001	NT	0.074	0.158
18	NT	NT	NT	NT	0.0036	0.0003	0.0002	NT	NT	NT	NT
19	NT	0.029	0.001	NT	0.008	0.0003	0.0035	0.02	NT	NT	NT
20	0.012	0.011	0.0012	0.14	0.0046	0.00035	<0.0001	0.00022	NT	0.067	0.11
21	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT

*All values are in units of mg/L. AV = Assigned Value, NT = Not Tested. Shaded cells are results which returned a questionable or not acceptable z-score.

Table 38 Summary of Participants' Results and Performance for Sample S2*

Lab. Code	Acephate	Atrazine	Bromacil	2,4-D	Fipronil	MCPA	Total Metolachlor	Metsulfuron-methyl	Picloram	Pirimicarb	Propazine	Triadimefon
AV	Not Set	Not Set	0.69	0.0426	Not Set	0.0401	0.530	0.060	1.12	0.0057	Not Set	Not Set
1	NT	0.0263	0.743	0.0517	NT	0.0561	0.604	NT	1.35	0.00785	0.000184	NT
2	NT	0.015	0.3469	NT	NT	NT	0.5318	NT	NT	NT	<0.00005	NT
3	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
4	NT	0.025	0.710	0.040	0.00118	0.037	0.575	0.063	1.191	NT	0.000155	NT
5	NT	0.0296	NT	0.0343	0.00145	0.0340	0.671	0.072	0.992	0.00683	NT	0.0925
6	0.0083	0.019	0.83	0.037	0.00083	0.034	0.48	0.06	0.90	0.0049	0.00016	0.087
7	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
9	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
10	NT	0.020	0.62	0.044	0.0012	0.041	0.56	0.054	0.46	0.0057	< 0.0001	0.054
11	NT	0.0112	0.39	0.0514	NT	0.0469	0.52	NT	1.42	0.004	<0.00009	0.0598
12	NT	0.024	0.672	0.044	NT	0.044	0.521	0.056	0.686	0.0062	0.00016	NT
13	NT	NT	NT	0.0407	NT	0.0426	NT	0.0575	1.07	NT	NT	NT
14	NT	0.0178	NT	NT	0.0013	NT	NT	NT	NT	NT	NT	NT
15	NT	0.025	NT	0.0338	NT	0.0366	0.3478	0.0335	0.9565	NT	< 0.002	NT
16	NT	0.0116	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
17	0.005	0.038	1.117	0.049	0.002	0.031	NT	NT	1.389	0.005	<0.002	0.102
18	NT	NT	NT	0.0431	NT	0.0435	NT	NT	1.19	NT	NT	NT
19	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
20	0.0077	0.020	0.60	NT	<0.002	NT	0.45	0.089	NT	0.0053	<0.001	0.098
21	NT	0.0321	0.9491	NT	NT	NT	1.1823	NT	NT	NT	<0.00005	NT

*All values are in units of mg/L. AV = Assigned Value, NT = Not Tested, NS = Not Supplied. Shaded cells are results which returned a questionable or not acceptable z-score.

Table 39 Summary of Participants' Results and Performance for Sample S3*

Lab. Code	AMPA	Glyphosate
AV	0.00952	0.086
1	NT	0.0741
2	NS	NS
3	0.0092	0.069
4	NT	NT
5	NT	NT
6	0.010	0.095
7	NS	NS
9	NS	NS
10	0.011	0.064
11	NT	NT
12	0.009	0.098
13	0.009	0.084
14	0.0096	0.0888
15	NS	NS
16	NT	NT
17	<0.1	0.119
18	NS	NS
19	NS	NS
20	0.0094	0.087
21	NS	NS

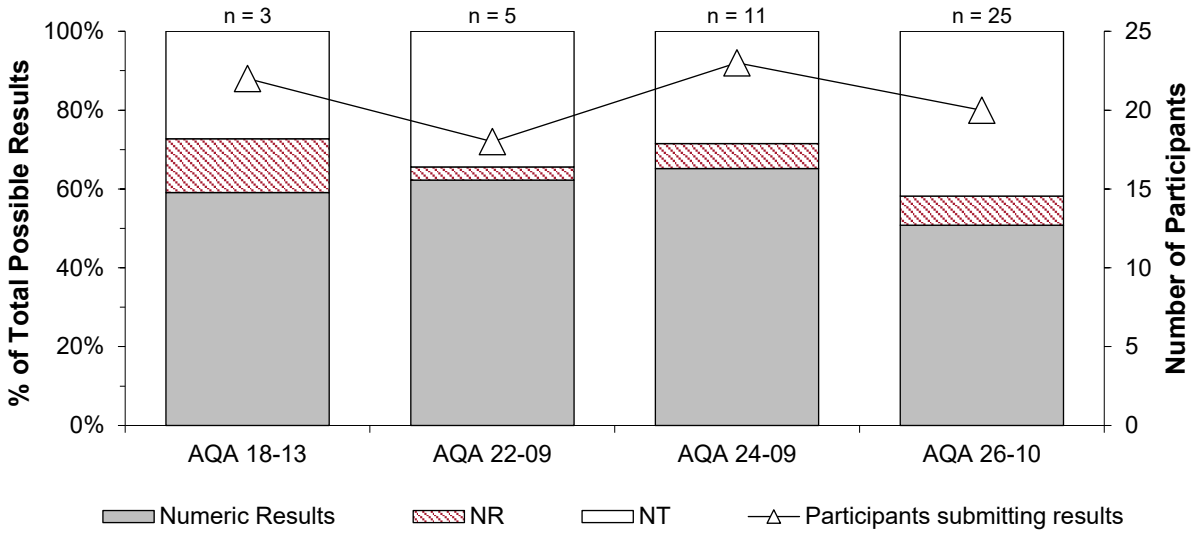
*All values are in units of mg/L. AV = Assigned Value, NT = Not Tested, NS = Not Supplied. Shaded cells are results which returned a questionable or not acceptable z-score.

6.11 Comparison with Previous Pesticides in Potable Water PT Studies

A summary of the participation and reported results in NMIA pesticides in potable water studies is presented in Figure 67. There was an increase in the number of analytes not being tested by participants in this study, though the significantly increased number of pesticides being assessed may have contributed to this.

A summary of the acceptable performance obtained by participants in NMIA pesticides in potable water studies is presented in Figure 68. To enable direct comparison, the SDPA used to calculate z-scores has been kept constant at 15% PCV. Over this period, the average proportion of acceptable z-scores and E_n-scores was 87% and 82% respectively.

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



n = number of spiked analytes

Figure 67 Summary of Participation and Reported Results in NMIA Pesticides in Potable Water PT Studies

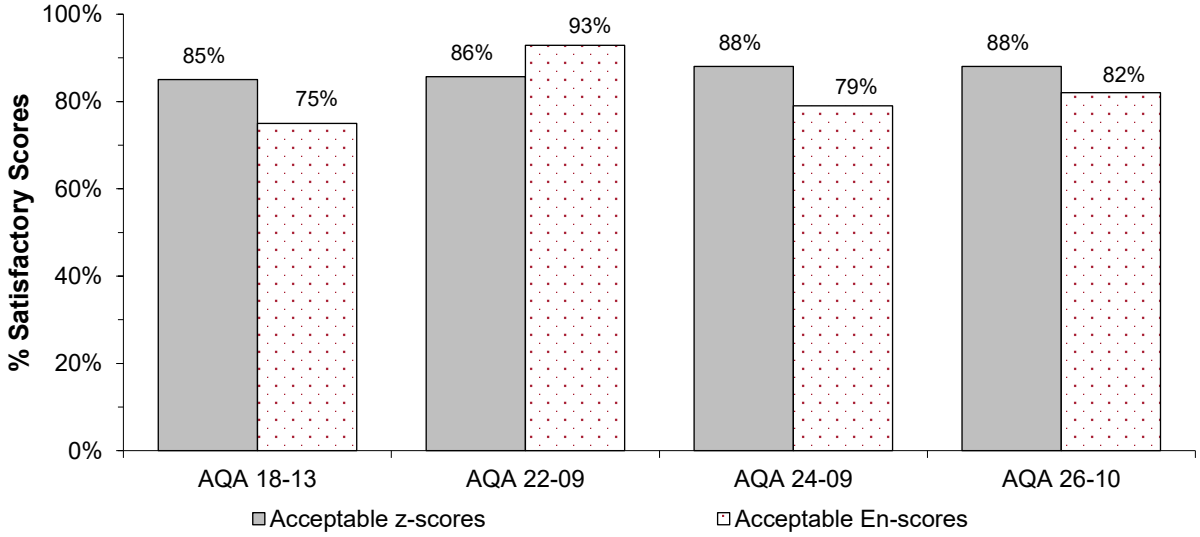


Figure 68 Acceptable z-Scores and E_n-Scores in NMIA Pesticides in Potable Water PT Studies

As discussed in Section 6.2, it is a requirement of ISO/IEC 17025 that laboratories report their uncertainties.[8] Figure 69 presents a summary of the relative uncertainties as reported by participants in NMIA pesticides in potable water samples. Over this period, the vast majority of numeric results were reported with uncertainties. Most relative uncertainties were between 15% and 50%. However, an average of 25% of relative uncertainties in each study were outside this range; these may have been unrealistically small or too large to be fit-for-purpose.

This study had both the highest proportion of relative uncertainties between 15% and 50%, and the lowest proportion of results reported without a MU, reflecting improved uncertainty evaluation and reporting practices by laboratories.

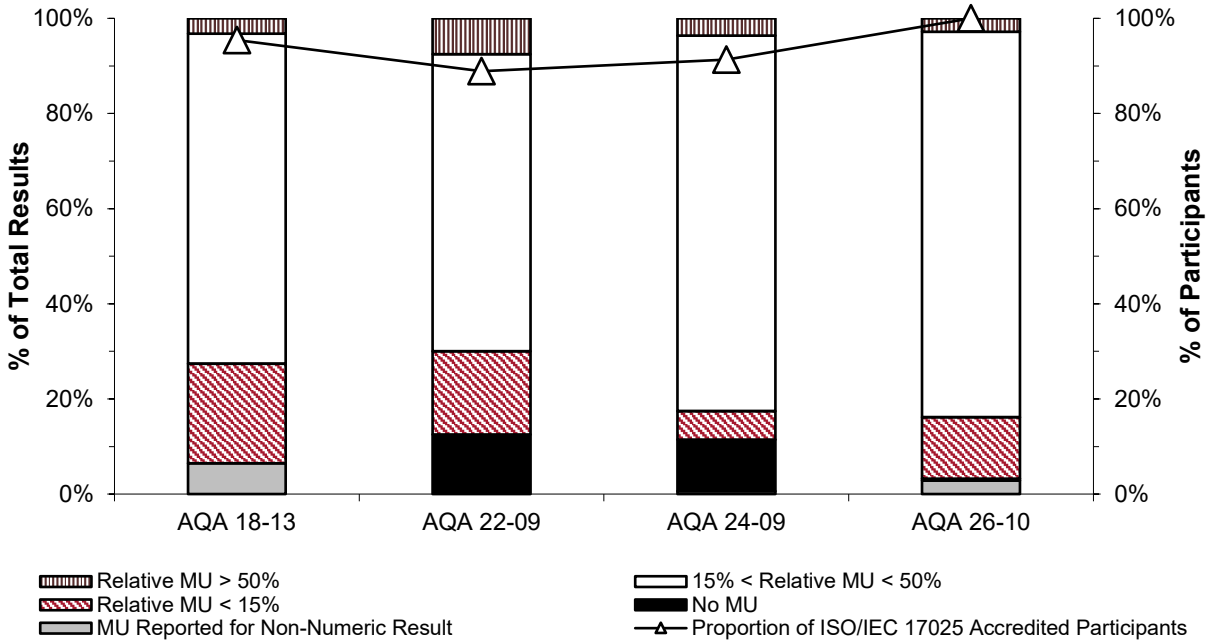


Figure 69 Summary of Participants' Relative Uncertainties for NMIA Pesticides in Potable Water PT Studies

7 REFERENCES

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

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APPENDIX 1 SAMPLE PREPARATION

All 3 samples were prepared using tap water (potable water) which was autoclaved prior to spiking.

The autoclaved water was spiked with pesticide standard solutions and then mixed.

Samples S1 and S2 were dispensed into amber glass bottles as 100 mL and 500 mL portions. Sample S3 was dispensed into plastic amber bottles as 500 mL portions only.

All samples were stored at 4 ºC until sample dispatch.

APPENDIX 2 ASSESSMENT OF HOMOGENEITY AND STABILITY

A2.1 Homogeneity

No homogeneity testing was completed for this study as the samples were prepared using a process previously demonstrated to produce sufficiently homogeneous samples. Participants' results in this study also gave no reason to question the samples' homogeneity.

A2.2 Stability

No stability testing was conducted for this study as the samples were prepared, stored and dispatched using a process previously demonstrated to produce sufficiently stable samples. After preparation and before dispatch, the samples were stored at 4 °C. For dispatch, samples were packaged into insulated polystyrene foam boxes with cooler bricks.

The results of this study also gave no reason to question the samples' transportation stability. For one participant, their samples were in transit for 6 days; for all other participants, samples were delivered within 2 days.

Comparisons of results to days spent in transit for scored analytes are presented in Figures 70 to 83 (solid blue lines correspond to the AV ± U). No significant instability was observed.

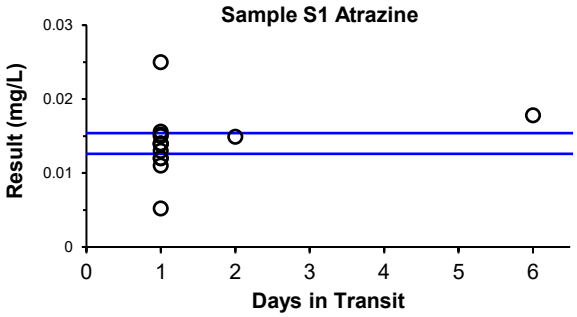

Figure 70 S1 Atrazine Results vs Transit Days

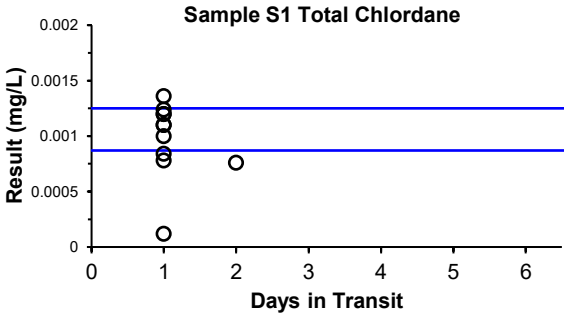

Figure 71 S1 Total Chlordane Results vs Transit Days

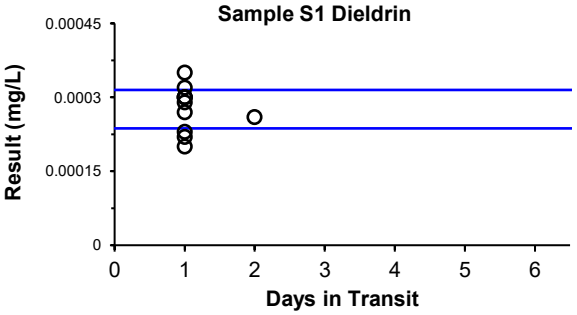

Figure 72 S1 Dieldrin Results vs Transit Days

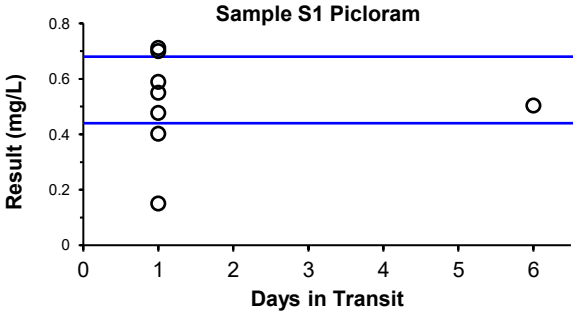

Figure 73 S1 Picloram Results vs Transit Days

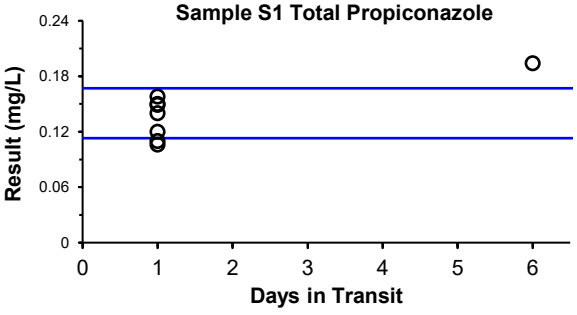

Figure 74 S1 Total Propiconazole Results vs Transit Days

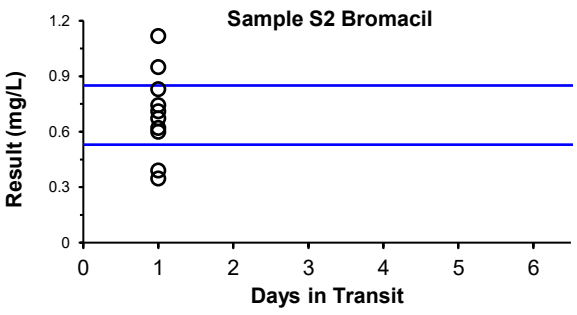

Figure 75 S2 Bromacil Results vs Transit Days

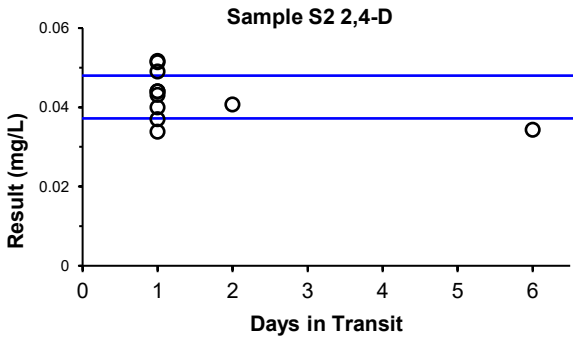

Figure 76 S2 2,4-D Results vs Transit Days

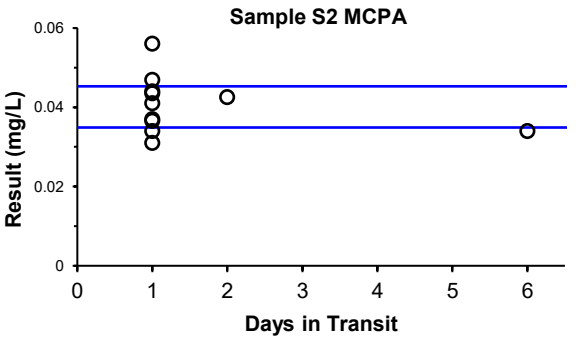

Figure 77 S2 MCPA Results vs Transit Days

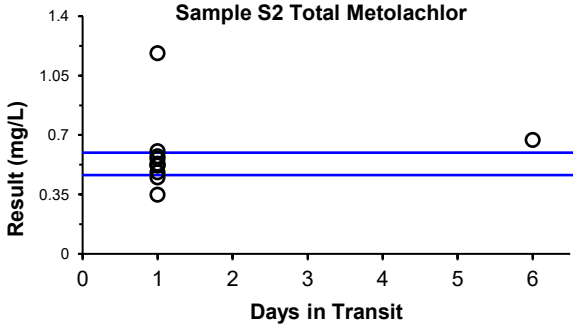

Figure 78 S2 Total Metolachlor Results vs Transit Days

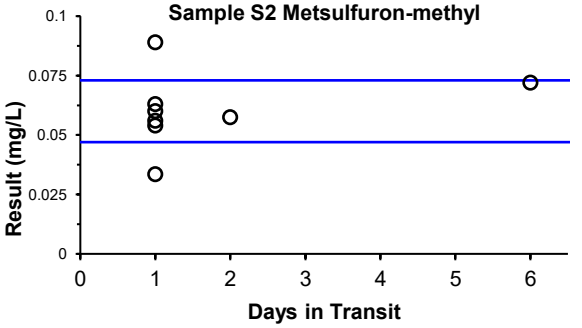

Figure 79 S2 Metsulfuron-methyl Results vs Transit Days

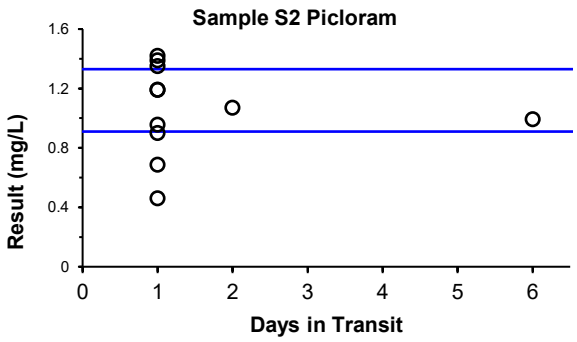

Figure 80 S2 Picloram Results vs Transit Days

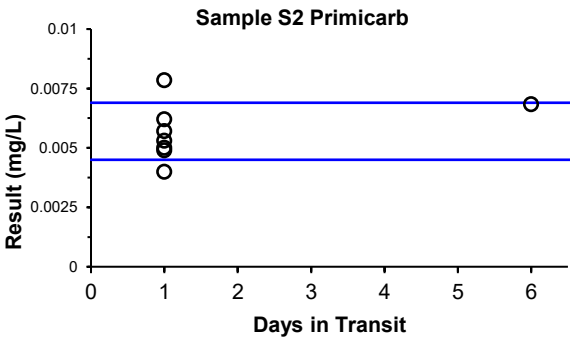

Figure 81 S2 Primicarb Results vs Transit Days

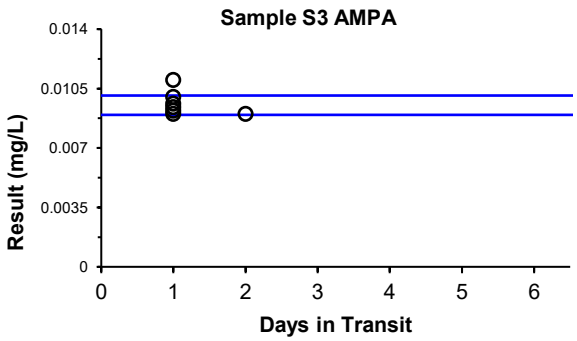

Figure 82 S3 AMPA Results vs Transit Days

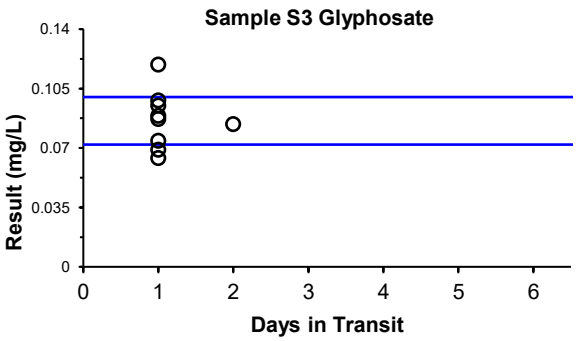

Figure 83 S3 Glyphosate Results vs Transit Days

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

A3.1 Robust Average and Associated Uncertainty

Robust averages were calculated using the procedure described in ISO 13528.[6] The associated uncertainties were evaluated as according to Equation 4.

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

where:

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

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

p is the number of results

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

A worked example for Sample S2 MCPA is set out below in Table 40.

Table 40 Uncertainty of Robust Average for Sample S2 MCPA

Number of results (p)	11
Robust Average	0.0401 mg/L
$S_{rob\ av}$	0.0068 mg/L
$u_{rob\ av}$	0.0026 mg/L
k	2
$U_{rob\ av}$	0.0052 mg/L

Therefore, the robust average for Sample S2 MCPA is 0.0401 ± 0.0052 mg/L.

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 10 for Sample S2 MCPA is set out below in Table 41.

Table 41 z-Score and E_n-Score Calculation for Sample S2 MCPA Result Reported by Laboratory 10

Participant Result (mg/L)	Assigned Value (mg/L)	Standard Deviation for Proficiency Assessment	z-Score	E_n-Score
0.041 ± 0.0123	0.0401 ± 0.0052	15% as PCV, or: 0.15 × 0.0401 = 0.006015 mg/L	$z = \frac{0.041 - 0.0401}{0.006015} = 0.15$	$E_n = \frac{0.041 - 0.0401}{\sqrt{0.0123^2 + 0.0052^2}} = 0.07$

APPENDIX 4 PARTICIPANTS' TEST METHODS

A4.1 METHODOLOGY FOR S1

Table 42 Measurement Methods and Instrument Techniques for Sample S1 Atrazine

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl
4	2	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	Yes, Atrazine-D5
5	4	No	No	Dilution	Acetonitrile: Methanol		10			Filtration	LC-MS/MS	
6	100	No	Yes, before sample extraction	Liquid-Liquid	DCM	3x25 mL	60	35	30	No clean up	GC-MS/MS	Yes, acenaphthene-d10 and chrysene-d12
10	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2 mL	10	21	10	None	GC-MS/MS	Yes, 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12
11	30	No	Yes, before sample extraction	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5mls and step 3: 5mls	45	40	Not set	N/A	GC-MS	Yes, in-house ISTD mix

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
12	10	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	diazinon-d10, atrazine-d5,dimethoate-d6,dichlorvos-d6,linuron-d6,carbaryl-d7
13	100	No	Yes, before sample extraction	SPE (Reverse Phase)	Acetone	2 mL x 1	NA	Ambient	NA	None	GC-MS/MS	yes, triphenyl phosphate
14	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	30	85	5	N/A	GC-MS	Yes, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene - d12, Perylene-d12
15	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 30 mL	3	35	30 (Approx.)	No	GC-MS/MS	Yes, Bromonitrobenzene and Bromophos-ethyl
16	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	2 / step	40	20	N/A	GC-MS	Yes, various
17	100 mL	No	No	Liquid-Liquid	DCM	3 x 20 mL	1.5	38		None	LC-MS/MS	Yes,TPP
20	50	No	Yes, before sample extraction	Liquid-Liquid	DCM	2x8mL	10	70		None	GC-MS/MS	13C12PCB Congener 1, 52, 138, 209

Table 43 Measurement Methods and Instrument Techniques for Sample S1 Azinphos-methyl

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl
5	4	No	No	Dilution	Acetonitrile: Methanol		10			Filtration	LC-MS/MS	
6	100	No	Yes, before sample extraction	Liquid-Liquid	DCM	3x25 mL	60	35	30	No clean up	GC-MS/MS	Yes, acenaphthene-d10 and chrysene-d12
7	35	Yes, bottle rinsed	Before adding solvent	Liquid-Liquid	DCM	2 x 35 mL	30	45	30	None	GC/MS/MS	Yes. Bromonitrobenzene
10	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2 mL	10	21	10	None	GC-MS/MS	Yes, 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12
11	30	No	Yes, before sample extraction	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5mls and step 3: 5mls	45	40	Not set	N/A	GC-MS	Yes, in-house ISTD mix
12	10	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	diazinon-d10, atrazine-d5,dimethoate-d6,dichlorvos-d6,linuron-d6,carbaryl-d7

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
13	100	No	Yes, before sample extraction	SPE (Reverse Phase)	Acetone	2 mL x 1	NA	Ambient	NA	None	GC-MS/MS	yes, triphenyl phosphate
14	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	30	85	5	N/A	GC-MS	Yes, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene -d12, Perylene-d12
15	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 30 mL	3	35	30 (Approx.)	No	GC-MS/MS	Yes, Bromonitrobenzene and Bromophos-ethyl
16	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	2 / step	40	20	N/A	GC-MS	Yes, various
17	100 mL	No	No	Liquid-Liquid	DCM	3 x 20 mL	1.5	38		None	LC-MS/MS	Yes,TPP
19	100	Yes, bottle NOT rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 15 mL	30	35	30		GC-MS	Yes, deuterated PAH
20	50	No	Yes, before sample extraction	Liquid-Liquid	DCM	2x8mL	10	70		None	GC-MS/MS	13C12PCB Congener 1, 52, 138, 209

Table 44 Measurement Methods and Instrument Techniques for Sample S1 Total Chlordane

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl
6	100	No	Yes, before sample extraction	Liquid-Liquid	DCM	3x25 mL	60	35	30	No clean up	GC-MS/MS	Yes, acenaphthene-d10 and chrysene-d12
7	35	Yes, bottle rinsed	Before adding solvent	Liquid-Liquid	DCM	2 x 35 mL	30	45	30	None	GC/MS/MS	Yes. Bromonitrobenzene
10	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2 mL	10	21	10	None	GC-MS/MS	Yes, 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12
11	30	No	Yes, before sample extraction	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5mls and step 3: 5mls	45	40	Not set	N/A	GC-ECD	Yes, 2,4,6-tribromobiphenyl
12	500	Yes, bottle NOT rinsed	Yes, before sample extraction	SPE (Reverse Phase)	DCM: EtOAc 1:1	2 x 5ml					GC-MS	phenanthrene-d10
13	100	No	Yes, before sample extraction	Liquid-Liquid	Hexane	2 mL x 2	2	Ambient	N A	None	GC-MS/MS	yes, quintozene, triphenyl phosphate

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
14	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	30	85	5	N/A	GC-MS	Yes, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene - d12, Perylene-d12
15	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 30 mL	3	35	30 (Approx.)	No	GC-MS/MS	Yes, Bromonitrobenzene and Bromophos-ethyl
16	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	2 / step	40	20	N/A	GC-MS	Yes, various
17	100 mL	No	No	Liquid-Liquid	DCM	3 x 20 mL	1.5	38		None	GC-MS/MS	Yes, Phenathrene d10
19	100	Yes, bottle NOT rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 15 mL	30	35	30		GC-MS	Yes, deuterated PAH
20	50	No	Yes, before sample extraction	Liquid-Liquid	DCM	2x8mL	10	70		None	GC-MS/MS	13C12PCB Congener 1, 52, 138, 209

Table 45 Measurement Methods and Instrument Techniques for Sample S1 Total Cypermethrin

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl
6	100	No	Yes, before sample extraction	Liquid-Liquid	DCM	3x25 mL	60	35	30	No clean up	GC-MS/MS	Yes, acenaphthene-d10 and chrysene-d12
10	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2 mL	10	21	10	None	GC-MS/MS	Yes, 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12
11	30	No	Yes, before sample extraction	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5mls and step 3: 5mls	45	40	Not set	N/A	GC-MS	Yes, in-house ISTD mix
12	500	Yes, bottle NOT rinsed	Yes, before sample extraction	SPE (Reverse Phase)	DCM: EtOAc 1:1	2 x 5ml					GC-MS	phenanthrene-d10
14	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	30	85	5	N/A	GC-MS	Yes, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene -d12, Perylene-d12
15	100	Yes, bottle rinsed	No	Liquid-Liquid	Acetonitrile	1 x 50 mL, 1 x 35 mL, 1 x 25 mL	60	35	60 (Approx.)	No	HPLC-DAD	No

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
16	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	2 / step	40	20	N/A	GC-MS	Yes, various
20	50	No	Yes, before sample extraction	Liquid-Liquid	DCM	2x8mL	10	70		None	GC-MS/MS	13C12PCB Congener 1, 52, 138, 209

Table 46 Measurement Methods and Instrument Techniques for Sample S1 p,p'-DDT

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl
6	100	No	Yes, before sample extraction	Liquid-Liquid	DCM	3x25 mL	60	35	30	No clean up	GC-MS/MS	Yes, acenaphthene-d10 and chrysene-d12
7	35	Yes, bottle rinsed	Before adding solvent	Liquid-Liquid	DCM	2 x 35 mL	30	45	30	None	GC/MS/MS	Yes. Bromonitrobenzene
10	35	No	Yes, before	Liquid-Liquid	DCM	2 x 2 mL	10	21	10	None	GC-MS/MS	Yes, 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10,

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
			sample extraction									Phenanthrene-d10, Chrysene-d12, Perylene-d12
11	30	No	Yes, before sample extraction	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5mls and step 3: 5mls	45	40	Not set	N/A	GC-ECD	Yes, 2,4,6-tribromobiphenyl
12	500	Yes, bottle NOT rinsed	Yes, before sample extraction	SPE (Reverse Phase)	DCM: EtOAc 1:1	2 x 5ml					GC-MS	phenanthrene-d10
13	100	No	Yes, before sample extraction	Liquid-Liquid	Hexane	2 mL x 2	2	Ambient	N A	None	GC-MS/MS	yes, quintozene, triphenyl phosphate
14	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	30	85	5	N/A	GC-MS	Yes, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene - d12, Perylene-d12
15	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 30 mL	3	35	30 (Approx.)	No	GC-MS/MS	Yes, Bromonitrobenzene and Bromophos-ethyl
16	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	2 / step	40	20	N/A	GC-MS	Yes, various
17	100 mL	No	No	Liquid-Liquid	DCM	3 x 20 mL	1.5	38		None	GC-MS/MS	Yes, Phenathrene d10
18	40	No	Yes, before	Liquid-Liquid	Hexane	3 x 5 mL	NA	30	NA	NA	GC-MS/MS	Yes, PBB-7 and PBB-18

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
			sample extraction									
19	100	Yes, bottle NOT rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 15 mL	30	35	30		GC-MS	Yes, deuterated PAH
20	50	No	Yes, before sample extraction	Liquid-Liquid	DCM	2x8mL	10	70		None	GC-MS/MS	13C12PCB Congener 1, 52, 138, 209

Table 47 Measurement Methods and Instrument Techniques for Sample S1 Dieldrin

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl
6	100	No	Yes, before sample extraction	Liquid-Liquid	DCM	3x25 mL	60	35	30	No clean up	GC-MS/MS	Yes, acenaphthene-d10 and chrysene-d12
7	35	Yes, bottle rinsed	Before adding solvent	Liquid-Liquid	DCM	2 x 35 mL	30	45	30	None	GC/MS/MS	Yes. Bromonitrobenzene

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
10	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2 mL	10	21	10	None	GC-MS/MS	Yes, 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12
11	30	No	Yes, before sample extraction	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5mls and step 3: 5mls	45	40	Not set	N/A	GC-ECD	Yes, 2,4,6-tribromobiphenyl
12	500	Yes, bottle NOT rinsed	Yes, before sample extraction	SPE (Reverse Phase)	DCM: EtOAc 1:1	2 x 5ml					GC-MS	phenanthrene-d10
13	100	No	Yes, before sample extraction	Liquid-Liquid	Hexane	2 mL x 2	2	Ambient	N A	None	GC-MS/MS	yes, quintozene, triphenyl phosphate
14	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	30	85	5	N/A	GC-MS	Yes, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene -d12, Perylene-d12
15	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 30 mL	3	35	30 (Approx.)	No	GC-MS/MS	Yes, Bromonitrobenzene and Bromophos-ethyl
16	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	2 / step	40	20	N/A	GC-MS	Yes, various

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
17	100 mL	No	No	Liquid-Liquid	DCM	3 x 20 mL	1.5	38		None	GC-MS/MS	Yes, Phenathrene d10
18	40	No	Yes, before sample extraction	Liquid-Liquid	Hexane	3 x 5 mL	NA	30	NA	NA	GC-MS/MS	Yes, PBB-7 and PBB-18
19	100	Yes, bottle NOT rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 15 mL	30	35	30		GC-MS	Yes, deuterated PAH
20	50	No	Yes, before sample extraction	Liquid-Liquid	DCM	2x8mL	10	70		None	GC-MS/MS	13C12PCB Congener 1, 52, 138, 209

Table 48 Measurement Methods and Instrument Techniques for Sample S1 Total Endosulfan

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl
6	100	No	Yes, before sample extraction	Liquid-Liquid	DCM	3x25 mL	60	35	30	No clean up	GC-MS/MS	Yes, acenaphthene-d10 and chrysene-d12

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
7	35	Yes, bottle rinsed	Before adding solvent	Liquid-Liquid	DCM	2 x 35 mL	30	45	30	None	GC/MS/MS	Yes. Bromonitrobenzene
10	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2 mL	10	21	10	None	GC-MS/MS	Yes, 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12
11	30	No	Yes, before sample extraction	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5mls and step 3: 5mls	45	40	Not set	N/A	GC-ECD	Yes, 2,4,6-tribromobiphenyl
12	500	Yes, bottle NOT rinsed	Yes, before sample extraction	SPE (Reverse Phase)	DCM: EtOAc 1:1	2 x 5ml					GC-MS	phenanthrene-d10
13	100	No	Yes, before sample extraction	Liquid-Liquid	Hexane	2 mL x 2	2	Ambient	N A	None	GC-MS/MS	yes, quintozene, triphenyl phosphate
14	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	30	85	5	N/A	GC-MS	Yes, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene -d12, Perylene-d12
15	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 30 mL	3	35	30 (Approx.)	No	GC-MS/MS	Yes, Bromonitrobenzene and Bromophos-ethyl

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
16	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	2 / step	40	20	N/A	GC-MS	Yes, various
17	100 mL	No	No	Liquid-Liquid	DCM	3 x 20 mL	1.5	38		None	GC-MS/MS	Yes, Phenathrene d10
18	40	No	Yes, before sample extraction	Liquid-Liquid	Hexane	3 x 5 mL	NA	30	NA	NA	GC-MS/MS	Yes, PBB-7 and PBB-18
19	100	Yes, bottle NOT rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 15 mL	30	35	30		GC-MS	Yes, deuterated PAH
20	50	No	Yes, before sample extraction	Liquid-Liquid	DCM	2x8mL	10	70		None	GC-MS/MS	13C12PCB Congener 1, 52, 138, 209

Table 49 Measurement Methods and Instrument Techniques for Sample S1 Maldison

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
5	4	No	No	Dilution	Acetonitrile: Methanol		10			Filtration	LC-MS/MS	
6	100	No	Yes, before sample extraction	Liquid-Liquid	DCM	3x25 mL	60	35	30	No clean up	GC-MS/MS	Yes, acenaphthene-d10 and chrysene-d12
7	35	Yes, bottle rinsed	Before adding solvent	Liquid-Liquid	DCM	2 x 35 mL	30	45	30	None	GC/MS/MS	Yes.Bromophos-ethyl
10	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2 mL	10	21	10	None	GC-MS/MS	Yes, 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12
11	30	No	Yes, before sample extraction	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5mls and step 3: 5mls	45	40	Not set	N/A	GC-MS	Yes, in-house ISTD mix
12	10	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	diazinon-d10, atrazine-d5,dimethoate-d6,dichlorvos-d6,linuron-d6,carbaryl-d7
13	100	No	Yes, before sample extraction	SPE (Reverse Phase)	Acetone	2 mL x 1	NA	Ambient	NA	None	GC-MS/MS	yes, triphenyl phosphate

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
14	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	30	85	5	N/A	GC-MS	Yes, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene -d12, Perylene-d12
15	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 30 mL	3	35	30 (Approx.)	No	GC-MS/MS	Yes, Bromonitrobenzene and Bromophos-ethyl
16	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	2 / step	40	20	N/A	GC-MS	Yes, various
17	100 mL	No	No	Liquid-Liquid	DCM	3 x 20 mL	1.5	38		None	LC-MS/MS	Yes,TPP
19	100	Yes, bottle NOT rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 15 mL	30	35	30		GC-MS	Yes, deuterated PAH
20	50	No	Yes, before sample extraction	Liquid-Liquid	DCM	2x8mL	10	70		None	GC-MS/MS	13C12PCB Congener 1, 52, 138, 209

Table 50 Measurement Methods and Instrument Techniques for Sample S1 Picloram

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl
4	2	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	Yes, Atrazine-D5
5	4	No	No	Dilution	Methanol		10			Filtration	LC-MS/MS	
6	30	No	Yes, before sample extraction	Liquid-Liquid	MTBE	4x3 mL	15	40	30	No clean up	GC-MS	Yes, 4,4-dibromooctafluoro biphenyl
7	35	Yes, bottle rinsed	Before adding solvent	Liquid-Liquid	DCM	2 x 35 mL	30	45	30	None	GC/MS/MS	Yes.Bromophos-ethyl
10	30	No	Yes, before sample extraction	Liquid-Liquid + Diazomethane derivatization	DCM	1 x 3 mL	10	21	10	None	GC-MS/MS	Yes, Pyrene-d12
11	1	No	Yes, after sample extraction, before instrument analysis	Direct Injection	N/A	N/A	N/A	N/A	N/A	N/A	LC-MS/MS	No
12	10	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	2,4-D

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
15	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	30 % Diethyl Ether / 70 % DCM	3 x 25 mL	15	35	30 (Approx.)	No	HPLC-DAD	Monuron
16	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	2 / step	40	20	N/A	GC-MS	Yes, various

Table 51 Measurement Methods and Instrument Techniques for Sample S1 Pirimiphos-methyl

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl
5	4	No	No	Dilution	Acetonitrile: Methanol		10			Filtration	LC-MS/MS	
10	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2 mL	10	21	10	None	GC-MS/MS	Yes, 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
11	30	No	Yes, before sample extraction	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5mls and step 3: 5mls	45	40	Not set	N/A	GC-MS	Yes, in-house ISTD mix
12	10	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	diazinon-d10, atrazine-d5,dimethoate-d6,dichlorvos-d6,linuron-d6,carbaryl-d7
15	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 30 mL	3	35	30 (Approx.)	No	GC-MS/MS	Yes, Bromonitrobenzene and Bromophos-ethyl
16	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	2 / step	40	20	N/A	GC-MS	Yes, various
17	100 mL	No	No	Liquid-Liquid	DCM	3 x 20 mL	1.5	38		None	GC-MS/MS	Yes, Phenathrene d10
20	50	No	Yes, before sample extraction	Liquid-Liquid	DCM	2x8mL	10	70		None	GC-MS/MS	13C12PCB Congener 1, 52, 138, 209

Table 52 Measurement Methods and Instrument Techniques for Sample S1 Total Propiconazole

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl
5	4	No	No	Dilution	Acetonitrile: Methanol		10			Filtration	LC-MS/MS	
6	10	No	Yes, before sample extraction	Direct Injection	-	-	-	-	-	No clean up	LC-MS/MS	Yes, diuron-d6
10	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2 mL	10	21	10	None	GC-MS/MS	Yes, 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12
11	30	No	Yes, before sample extraction	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5mls and step 3: 5mls	45	40	Not set	N/A	GC-MS	Yes, in-house ISTD mix
12	10	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	diazinon-d10, atrazine-d5,dimethoate-d6,dichlorvos-d6,linuron-d6,carbaryl-d7
16	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	2 / step	40	20	N/A	GC-MS	Yes, various

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
17	100 mL	No	No	Liquid-Liquid	DCM	3 x 20 mL	1.5	38		None	LC-MS/MS	Yes,TPP
20	50	No	Yes, before sample extraction	Liquid-Liquid	DCM	2x8mL	10	70		None	GC-MS/MS	13C12PCB Congener 1, 52, 138, 209

A4.2 METHODOLOGY FOR S2

Table 53 Measurement Methods and Instrument Techniques for S2 Acephate

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
2	500	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM/ EtOAc/ MeOH	15mL, 10 steps	30	35	25		GC-MS	Yes, Method 525.2 Internal Std Mix
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl
6	10	No	Yes, before sample extraction	Direct Injection	-	-	-	-	-	No clean up	LC-MS/MS	Yes, diuron-d6
11	30	No	Yes, before sample extraction	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5mls	45	40	Not set	N/A	GC-MS	Yes, in-house ISTD mix

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
						and step 3: 5mls						
12	10	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	diazinon-d10, atrazine-d5,dimethoate-d6,dichlorvos-d6,linuron-d6,carbaryl-d7
17	100 mL	No	No	Liquid-Liquid	DCM	3 x 20 mL	1.5	38		None	LC-MS/MS	Yes,TPP
20	5	No	Yes, before sample extraction	Direct Injection						Filtration	LC-MS/MS	Imidacloprid-d4, Pirimicarb-d6, Carbofuran-d3, Ispropturon-d6, Diuron-d6
21	500	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM/ EtOAc/ MeOH	15mL, 10 steps	30	35	25		GC-MS	Yes, Method 525.2 Internal Std Mix

Table 54 Measurement Methods and Instrument Techniques for S2 Atrazine

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
4	2	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	Yes, Atrazine-D5
5	4	No	No	Dilution	Acetonitrile: Methanol		10			Filtration	LC-MS/MS	
6	100	No	Yes, before sample extraction	Liquid-Liquid	DCM	3x25 mL	60	35	30	No clean up	GC-MS/MS	Yes, acenaphthene-d10 and chrysene-d12
10	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2 mL	10	21	10	None	GC-MS/MS	Yes, 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12
11	30	No	Yes, before sample extraction	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5mls and step 3: 5mls	45	40	Not set	N/A	GC-MS	Yes, in-house ISTD mix
12	10	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	diazinon-d10, atrazine-d5,dimethoate-d6,dichlorvos-d6,linuron-d6,carbaryl-d7
14	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	30	85	5	N/A	GC-MS	Yes, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene -d12, Perylene-d12

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
15	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 30 mL	3	35	30 (Approx.)	No	GC-MS/MS	Yes, Bromonitrobenzene and Bromophos-ethyl
16	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	2 / step	40	20	N/A	GC-MS	Yes, various
17	100 mL	No	No	Liquid-Liquid	DCM	3 x 20 mL	1.5	38		None	LC-MS/MS	Yes,TPP
20	50	No	Yes, before sample extraction	Liquid-Liquid	DCM	2x8mL	10	70		None	GC-MS/MS	13C12PCB Congener 1, 52, 138, 209

Table 55 Measurement Methods and Instrument Techniques for S2 Bromacil

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl
4	2	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	Yes, Atrazine-D5

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
6	10	No	Yes, before sample extraction	Direct Injection	-	-	-	-	-	No clean up	LC-MS/MS	Yes, diuron-d6
10	1	No	No	Direct Injection	NA	NA	NA	21	10	None	LC-MS/MS	Yes, Carbaryl-d3, Linuron-d6, Propachlor-d5, Monuron-d6, Carbofuran-d3
11	30	No	Yes, before sample extraction	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5mls and step 3: 5mls	45	40	Not set	N/A	GC-MS	Yes, in-house ISTD mix
12	500	Yes, bottle NOT rinsed	Yes, before sample extraction	SPE (Reverse Phase)	DCM: EtOAc 1:1	2 x 5ml					GC-MS	phenanthrene-d10
17	100 mL	No	No	Liquid-Liquid	DCM	3 x 20 mL	1.5	38		None	LC-MS/MS	Yes,TPP
20	5	No	Yes, before sample extraction	Direct Injection						Filtration	LC-MS/MS	Imidacloprid-d4, Pirimicarb-d6, Carbofuran-d3, Ispropturon-d6, Diuron-d6

Table 56 Measurement Methods and Instrument Techniques for S2 2,4-D

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl
4	2	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	Yes, Atrazine-D5
5	4	No	No	Dilution	Methanol		10			Filtration	LC-MS/MS	
6	30	No	Yes, before sample extraction	Liquid-Liquid	MTBE	4x3 mL	15	40	30	No clean up	GC-MS	Yes, 4,4-dibromooctafluorobiphenyl
10	30	No	Yes, before sample extraction	Liquid-Liquid + Diazomethane derivatization	DCM	1 x 3 mL	10	21	10	None	GC-MS/MS	Yes, Pyrene-d12
11	1	No	Yes, after sample extraction, before instrument analysis	Direct Injection	N/A	N/A	N/A	N/A	N/A	N/A	LC-MS/MS	No
12	10	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	2,4-D
13	1	No	Yes, before sample extraction	Direct Injection	NA	NA	NA	Ambient	NA	Filtration	LC-MS/MS	No

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
15	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	30 % Diethyl Ether / 70 % DCM	3 x 25 mL	15	35	30 (Approx.)	No	HPLC-DAD	Monuron
17	10 mL	No	No	Hydrolysed with KOH, neutralised and injected							LC-MS/MS	Yes, Dichlorophenylacetic acid
18	0.95	No	Yes, before sample extraction	Direct Injection	Methanol	NA	NA	NA	NA	NA	LC-MS/MS	Yes, Dichlorprop, 2,4,5-T and PCP

Table 57 Measurement Methods and Instrument Techniques for S2 Fipronil

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl
4	2	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	Yes, Atrazine-D5
5	4	No	No	Dilution	Acetonitrile: Methanol		10			Filtration	LC-MS/MS	

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
6	10	No	Yes, before sample extraction	Direct Injection	-	-	-	-	-	No clean up	LC-MS/MS	Yes, diuron-d6
10	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2 mL	10	21	10	None	GC-MS/MS	Yes, 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12
14	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	3 x 6 mL	30	85	5	N/A	GC-MS	Yes, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene -d12, Perylene-d12
17	100 mL	No	No	Liquid-Liquid	DCM	3 x 20 mL	1.5	38		None	GC-MS/MS	Yes, Phenathrene d10
20	5	No	Yes, before sample extraction	Direct Injection						Filtration	LC-MS/MS	Imidacloprid-d4, Pirimicarb-d6, Carbofuran-d3, Ispropturon-d6, Diuron-d6

Table 58 Measurement Methods and Instrument Techniques for S2 MCPA

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl
4	2	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	Yes, Atrazine-D5
5	4	No	No	Dilution	Methanol		10			Filtration	LC-MS/MS	
6	30	No	Yes, before sample extraction	Liquid-Liquid	MTBE	4x3 mL	15	40	30	No clean up	GC-MS	Yes, 4,4-dibromooctafluorobiphenyl
10	30	No	Yes, before sample extraction	Liquid-Liquid + Diazomethane derivatization	DCM	1 x 3 mL	10	21	10	None	GC-MS/MS	Yes, Pyrene-d12
11	1	No	Yes, after sample extraction, before instrument analysis	Direct Injection	N/A	N/A	N/A	N/A	N/A	N/A	LC-MS/MS	No
12	10	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	2,4-D
13	1	No	Yes, before sample extraction	Direct Injection	NA	NA	NA	Ambient	NA	Filtration	LC-MS/MS	No

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
15	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	30 % Diethyl Ether / 70 % DCM	3 x 25 mL	15	35	30 (Approx.)	No	HPLC-DAD	Monuron
17	10 mL	No	No	Hydrolysed with KOH, neutralised and injected							LC-MS/MS	Yes, Dichlorophenylacetic acid
18	0.95	No	Yes, before sample extraction	Direct Injection	Methanol	NA	NA	NA	NA	NA	LC-MS/MS	Yes, Dichlorprop, 2,4,5-T and PCP

Table 59 Measurement Methods and Instrument Techniques for S2 Total Metolachlor

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl
4	2	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	Yes, Atrazine-D5
5	4	No	No	Dilution	Acetonitrile: Methanol		10			Filtration	LC-MS/MS	

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
6	10	No	Yes, before sample extraction	Direct Injection	-	-	-	-	-	No clean up	LC-MS/MS	Yes, diuron-d6
10	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2 mL	10	21	10	None	GC-MS/MS	Yes, 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12
11	30	No	Yes, before sample extraction	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5mls and step 3: 5mls	45	40	Not set	N/A	GC-MS	Yes, in-house ISTD mix
12	10	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	diazinon-d10, atrazine-d5,dimethoate-d6,dichlorvos-d6,linuron-d6,carbaryl-d7
15	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	30 % Diethyl Ether / 70 % DCM	3 x 25 mL	15	35	30 (Approx.)	No	HPLC-DAD	Monuron
20	5	No	Yes, before sample extraction	Direct Injection						Filtration	LC-MS/MS	Imidacloprid-d4, Pirimicarb-d6, Carbofuran-d3, Ispropturon-d6, Diuron-d6

Table 60 Measurement Methods and Instrument Techniques for S2 Metsulfuron-methyl

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl
4	2	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	Yes, Atrazine-D5
5	4	No	No	Dilution	Acetonitrile : Methanol		10			Filtration	LC-MS/MS	
6	10	No	Yes, before sample extraction	Direct Injection	-	-	-	-	-	No clean up	LC-MS/MS	Yes, diuron-d6
10	30	No	Yes, before sample extraction	Liquid-Liquid + Diazomethane derivatization	DCM	1 x 3 mL	10	21	10	None	GC-MS/MS	Yes, Pyrene-d12
12	10	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	diazinon-d10, atrazine-d5,dimethoate-d6,dichlorvos-d6,linuron-d6,carbaryl-d7
13	1	No	Yes, before sample extraction	Direct Injection	NA	NA	NA	Ambient	NA	Filtration	LC-MS/MS	No
15	100	Yes, bottle rinsed	Yes, before	Liquid-Liquid	30 % Diethyl	3 x 25 mL	15	35	30 (Approx.)	No	HPLC-DAD	Monuron

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
			sample extraction		Ether / 70 % DCM							
20	5	No	Yes, before sample extraction	Direct Injection						Filtration	LC-MS/MS	Imidacloprid-d4, Pirimicarb-d6, Carbofuran-d3, Ispropturon-d6, Diuron-d6

Table 61 Measurement Methods and Instrument Techniques for S2 Picloram

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl
4	2	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	Yes, Atrazine-D5
5	4	No	No	Dilution	Methanol		10			Filtration	LC-MS/MS	
6	30	No	Yes, before sample extraction	Liquid-Liquid	MTBE	4x3 mL	15	40	30	No clean up	GC-MS	Yes, 4,4-dibromooctafluorobiphenyl
10	30	No	Yes, before	Liquid-Liquid +	DCM	1 x 3 mL	10	21	10	None	GC-MS/MS	Yes, Pyrene-d12

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
			sample extraction	Diazomethane derivatization								
11	1	No	Yes, after sample extraction, before instrument analysis	Direct Injection	N/A	N/A	N/A	N/A	N/A	N/A	LC-MS/MS	No
12	10	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	2,4-D
13	1	No	Yes, before sample extraction	Direct Injection	NA	NA	NA	Ambient	NA	Filtration	LC-MS/MS	No
15	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	30 % Diethyl Ether / 70 % DCM	3 x 25 mL	15	35	30 (Approx.)	No	HPLC-DAD	Monuron
17	10 mL	No	No	Hydrolysed with KOH, neutralised and injected							LC-MS/MS	Yes, Dichlorophenylacetic acid
18	0.95	No	Yes, before sample extraction	Direct Injection	Methanol	NA	NA	NA	NA	NA	LC-MS/MS	Yes, Dichlorprop, 2,4,5-T and PCP

Table 62 Measurement Methods and Instrument Techniques for S2 Pirimicarb

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl
5	4	No	No	Dilution	Acetonitrile: Methanol		10			Filtration	LC-MS/MS	
6	10	No	Yes, before sample extraction	Direct Injection	-	-	-	-	-	No clean up	LC-MS/MS	Yes, diuron-d6
10	1	No	No	Direct Injection	NA	NA	NA	21	10	None	LC-MS/MS	Yes, Carbaryl-d3, Linuron-d6, Propachlor-d5, Monuron-d6, Carbofuran-d3
11	30	No	Yes, before sample extraction	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5mls and step 3: 5mls	45	40	Not set	N/A	GC-MS	Yes, in-house ISTD mix
12	10	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	diazinon-d10, atrazine-d5,dimethoate-d6,dichlorvos-d6,linuron-d6,carbaryl-d7
17	100 mL	No	No	Liquid-Liquid	DCM	3 x 20 mL	1.5	38		None	LC-MS/MS	Yes,TPP
20	5	No	Yes, before	Direct Injection						Filtration	LC-MS/MS	Imidacloprid-d4, Pirimicarb-d6, Carbofuran-d3,

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
			sample extraction									Ispropturon-d6, Diuron-d6

Table 63 Measurement Methods and Instrument Techniques for S2 Propazine

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl
4	2	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	Yes, Atrazine-D5
6	100	No	Yes, before sample extraction	Liquid-Liquid	DCM	3x25 mL	60	35	30	No clean up	GC-MS/MS	Yes, acenaphthene-d10 and chrysene-d12
10	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2 mL	10	21	10	None	GC-MS/MS	Yes, 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12
11	30	No	Yes, before	Liquid-Liquid	DCM	Step 1: 10mls, step	45	40	Not set	N/A	GC-MS	Yes, in-house ISTD mix

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
			sample extraction			2: 5mls and step 3: 5mls						
12	10	No	Yes, before sample extraction	Direct Injection							LC-MS/MS	diazinon-d10, atrazine-d5,dimethoate-d6,dichlorvos-d6,linuron-d6,carbaryl-d7
15	100	Yes, bottle rinsed	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 30 mL	3	35	30 (Approx.)	No	GC-MS/MS	Yes, Bromonitrobenzene and Bromophos-ethyl
17	100 mL	No	No	Liquid-Liquid	DCM	3 x 20 mL	1.5	38		None	LC-MS/MS	Yes,TPP
20	5	No	Yes, before sample extraction	Direct Injection						Filtration	LC-MS/MS	Imidacloprid-d4, Pirimicarb-d6, Carbofuran-d3, Ispropturon-d6, Diuron-d6

Table 64 Measurement Methods and Instrument Techniques for S2 Triadimefon

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	35	No	Yes, before	Liquid-Liquid	DCM	2 x 2ml	10	35	3		GC-MS/MS	Bromonitrobenzene and Bromophos ethyl

Lab. Code	Sample Volume (mL)	Was the entire bottle used? If yes, was the bottle rinsed?	Was surrogate used? If yes, when was it added?	Extraction Technique	Extraction Solvent	Extraction Volume and Number of Steps	Extraction Time (min)	Extract Concentration Temperature (°C)	Extract Concentration Time (min)	Extract Clean-Up	Measurement Technique	Were internal standards used? If yes, what internal standard?
			sample extraction									
5	4	No	No	Dilution	Acetonitrile: Methanol		10			Filtration	LC-MS/MS	
6	10	No	Yes, before sample extraction	Direct Injection	-	-	-	-	-	No clean up	LC-MS/MS	Yes, diuron-d6
10	35	No	Yes, before sample extraction	Liquid-Liquid	DCM	2 x 2 mL	10	21	10	None	GC-MS/MS	Yes, 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12
11	30	No	Yes, before sample extraction	Liquid-Liquid	DCM	Step 1: 10mls, step 2: 5mls and step 3: 5mls	45	40	Not set	N/A	GC-MS	Yes, in-house ISTD mix
17	100 mL	No	No	Liquid-Liquid	DCM	3 x 20 mL	1.5	38		None	LC-MS/MS	Yes,TPP
20	5	No	Yes, before sample extraction	Direct Injection						Filtration	LC-MS/MS	Imidacloprid-d4, Pirimicarb-d6, Carbofuran-d3, Ispropturon-d6, Diuron-d6

A4.3 METHODOLOGY FOR S3

Table 65 Measurement Methods and Instrument Techniques for S3 AMPA

Lab. Code	Sample Volume (mL)	If entire bottle used, was the bottle rinsed?	Extraction Technique	Derivatisation Procedure	Derivatisation Agent	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	1mL	N/A	Direct Injection	N/A	N/A	LC-MS	13C,15N-AMPA
6	1	No	Direct Injection	Pre-column	FMOC	LC-MS/MS	No
10	4	No	Direct Injection	Pre-column	fmoc Chloride	LC-MS/MS	AMPA(M+5)
12	10	N/A	Direct Injection			LC-MS/MS	AMPA -13c2-15N
13	0.4	No	Derivatization and Filtration			LC-FLD	No
14	1	N/A	Direct Injection	N/A	N/A	LC-MS/MS	13C15N AMPA
17	3						
20	5	No	Direct Injection	Pre-column	FMOC	LC-MS/MS	13C15N Glyphosate, 13C15N AMPA

Table 66 Measurement Methods and Instrument Techniques for S3 Glyphosate

Lab. Code	Sample Volume (mL)	If entire bottle used, was the bottle rinsed?	Extraction Technique	Derivatisation Procedure	Derivatisation Agent	Measurement Technique	Were internal standards used? If yes, what internal standard?
3	1mL	N/A	Direct Injection	N/A	N/A	LC-MS	D3-glufosinate
6	1	No	Direct Injection	Pre-column	FMOC	LC-MS/MS	No
10	4	No	Direct Injection	Pre-column	fmoc Chloride	LC-MS/MS	Glyphosate(M+3)
12	10	N/A	Direct Injection			LC-MS/MS	glyphosate-13C2-15N
13	0.4	No	Derivatization and Filtration			LC-FLD	No
14	1	N/A	Direct Injection	N/A	N/A	LC-MS/MS	13C2,15N Glyphosate
17	3						
20	5	No	Direct Injection	Pre-column	FMOC	LC-MS/MS	13C15N Glyphosate, 13C15N AMPA

APPENDIX 5 ACRONYMS AND ABBREVIATIONS

2,4-D	2,4-Dichlorophenoxyacetic acid
2,4,5-T	2,4,5-Trichlorophenoxyacetic acid
ACE	Acetone
ACN	Acetonitrile
ADWG	Australian Drinking Water Guidelines
AMPA	Aminomethylphosphonic acid
AV	Assigned Value
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
DAD	Diode Array Detection
DCM	Dichloromethane
DI	Direct Injection
ECD	Electron Capture Detection
EtOAc	Ethyl Acetate
FLD	Fluorescence Detection
FMOC	9-fluorenylmethoxycarbonyl
GC	Gas Chromatography
GUM	Guide to the Expression of Uncertainty in Measurement
HEX	Hexane
HPLC	High Performance Liquid Chromatography
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
k	Coverage Factor
LC	Liquid Chromatography
LLE	Liquid-Liquid Extraction
LOR	Limit of Reporting
Max	Maximum
MCPA	2-methyl-4-chlorophenoxyacetic acid
Md	Median
MeOH	Methanol
Min	Minimum
MS	Mass Spectrometry
MS/MS	Tandem Mass Spectrometry

MTBE	Methyl tert-butyl ether
MU	Measurement Uncertainty
N	Number of numeric results
NATA	National Association of Testing Authorities, Australia
NMIA	National Measurement Institute, Australia
NR	Not Reported
NS	Not Supplied
NT	Not Tested
PCV	Performance Coefficient of Variation
p,p'-DDT	p,p'-Dichlorodiphenyltrichloroethane
PT	Proficiency Testing
RA	Robust Average
Rec	Recovery
RM	Reference Material
s.f.	Significant Figures
SD	Standard Deviation
SDPA	Standard Deviation for Proficiency Assessment
SI	International System of Units
SPE	Solid Phase Extraction
SS	Spiked Samples
SV	Spiked Value (or formulated concentration of a PT sample)
U	Expanded Uncertainty

END OF REPORT