Fapas® – Food Chemistry Proficiency Test Report 19219

Pesticide Residues in Nectarine Purée

October-November 2016

PARTICIPANT LABORATORY NUMBER

Participants can log in to Fapas® SecureWeb at any time to obtain their laboratory number for this proficiency test.

Laboratory numbers are displayed in SecureWeb next to the download link for this report.

REPORT INTEGRITY

Fapas® reports are distributed as Adobe® Certified Document Services (CDS) Adobe® PDF documents [1]. The use of Adobe® CDS allows the PDF files to certify that the author of the report is Fapas® and that the document has not been altered in anyway. A blue ribbon and information bar indicates this validation when the document is opened using Adobe® Reader v7 or later.

Hard copies of Fapas® reports can never incorporate this level of integrity and consequently when a Fapas® report is printed a watermark, stating that printed copies are not controlled, appears on every page.

End users of Fapas® reports should ensure that either the opened PDF file displays a valid FAPAS digital signature or that the content of any hard copy exactly matches the content of a PDF file that displays a valid Fapas® digital signature.

QUALITY SYSTEMS

Fapas® – Food Chemistry is accredited by UKAS as complying with the requirements of ISO/IEC 17043:2010 [2].

Fera is an ISO 9001 certified organisation.

UKAS PROFICIENCY TESTING
0009

Fera hereby excludes all liability for any claim, loss, demands or damages of any kind whatsoever (whether such claims, loss, demands or damages were foreseeable, known or otherwise) arising out of or in connection with the preparation of any technical or scientific report, including without limitation, indirect or consequential loss or damage; loss of actual or anticipated profits (including loss of profits on contracts); loss of revenue; loss of business; loss of opportunity; loss of anticipated savings; loss of goodwill; loss of reputation; loss or damage to or corruption of data; loss of use of money or otherwise, and whether or not advised of the possibility of such claim, loss demand or damages and whether arising in tort (including negligence), contract or otherwise. This statement does not affect your statutory rights.

Nothing in this disclaimer excludes or limits Fera liability for: (a) death or personal injury caused by Fera negligence (or that of its employees, agents or directors); or (b) the tort of deceit; [or (c) any breach of the obligations implied by Sale of Goods Act 1979 or Supply of Goods and Services Act 1982 (including those relating to the title, fitness for purpose and satisfactory quality of goods);] or (d) any liability which may not be limited or excluded by law (e) fraud or fraudulent misrepresentation.

The parties agree that any matters are governed by English law and irrevocably submit to the non-exclusive jurisdiction of the English courts.

© Copyright Fera Science Ltd (Fera) 2016. All rights reserved.

SUMMARY

1. The test material for Fapas® – Food Chemistry proficiency test 19219 was dispatched in October 2016. Each participant received a nectarine purée test material.
2. From a list of 232 pesticide residues, participants had to identify and quantify those present. The test material contained carbendazim, cyprodinil, pp-DDD (TDE), endosulfan sulfate, fenbuconazole, pyrimethanil, tebuconazole and tetraconazole.
3. An assigned value (x_a) was determined for each analyte and in conjunction with the standard deviation for proficiency (σ_p) was used to calculate a z-score for each result.
4. Results for this proficiency test are summarised as follows:

analyte	assigned value, x_a µg/kg	number of scores, |z| ≤2	total number of scores	% |z| ≤2
carbendazim	66.0	30	41	73
cyprodinil	34.0	44	47	94
pp-DDD (TDE)	104	25	33	76
endosulfan sulfate	157	35	44	80
fenbuconazole	228	42	46	91
pyrimethanil	76.0	46	50	92
tebuconazole	87.1	47	49	96
tetraconazole	130	39	43	91

CONTENTS

1. INTRODUCTION

1.1. Proficiency Testing

Proficiency testing aims to provide an independent assessment of the competence of participating laboratories. Together with the use of validated methods, proficiency testing is an essential element of laboratory quality assurance.

Further details of the FAPAS – Food Chemistry proficiency testing scheme are available in our protocols [3, 4].

2. TEST MATERIAL

2.1. Preparation

Preparation of the samples for this proficiency test was sub-contracted to a laboratory meeting the quality requirements of the scheme's accreditation [2].

The test material was prepared from fresh nectarines, which were frozen and cryogenically milled. The bulk sample was split into two batches: one for spiking and one for the blank test material.

Sub-samples were taken to screen for the possible presence of incurred residues and the remainder was stored at -20°C.

No residues were detected at, or above, 15 µg/kg.

Carbendazim, cyprodinil, pp-DDD (TDE), endosulfan sulfate, fenbuconazole, pyrimethanil, tebuconazole and tetraconazole, were spiked into the test material.

Samples were stored at -20°C until dispatch.

2.2. Homogeneity

To test for homogeneity, randomly selected test materials were analysed in duplicate. Testing was sub-contracted to a laboratory meeting the quality requirements of the scheme's accreditation [2].

These data showed sufficient homogeneity and were not included in the subsequent calculation of the assigned values.

2.3. Dispatch

The start date was 18 October 2016. Test materials were sent to 61 participants.

3. RESULTS

The instructions for reporting results were as follows:

- Determine the level of pesticide residues present in the test material, in µg/kg, as received, uncorrected for recovery together, with the percentage recovery and limit of quantification (LoQ).

- All pesticide residues are to be reported as the parent compound only, unless specified otherwise on the results form. For permethrin, report your results as the sum of constituent isomers.
- If any residues are reported not in the form specified, please note this in the comments box.
- For residues tested for but not detected, please enter an LOQ via the 'review/resubmit your results' link on your list of tests. This has to be done after you have submitted results for all pesticide residues detected.
- This is an identification and quantification test, therefore if you analyse for a pesticide that is in the test material, and do not identify it, and your limit of quantification is below the level needed for a satisfactory z-score or you do not submit an LoQ, you will be assessed as if your result was zero.

Results were submitted by 54 participants (89%) before the closing date for this test, 24 November 2016.

Each participant was given a laboratory number, assigned in order of receipt of results. The reported analyte concentrations are given in Table 1-Table 3.

If a participant analysed for a pesticide residue that was in the test material, but did not identify it, and their LoQ (limit of quantification) was below the level needed for a z-score of -3.0 or an LoQ was not reported, they were assessed as if their result was zero.

If a participant analysed for a pesticide residue that was in the test material, but did not identify it and their LoQ was above the level needed for a z-score of -3.0, then the result was recorded as <LoQ.

Additional pesticides reported by participants, other than carbendazim, cyprodinil, pp-DDD (TDE), endosulfan sulfate, fenbuconazole, pyrimethanil, tebuconazole and tetraconazole are shown in Table 4.

Participants' comments are given in Table 5.

The analytical methods used by each participant are summarised in APPENDIX I.

4. STATISTICAL EVALUATION OF RESULTS

The results submitted by participants were statistically analysed in order to provide an assigned value for each analyte. The assigned values were then used in combination with the standard deviation for proficiency, σ_p, to calculate a z-score for each result. The procedure follows that recommended in the IUPAC International Harmonised Protocol for the Proficiency Testing of Analytical Chemistry Laboratories [5].

Further details on the procedure followed can be found in the relevant protocols [3, 4].

4.1. Calculation of the Assigned Value, x_a

The assigned value, x_a, for each analyte was derived from the consensus of the results submitted by participants.

The following results were excluded from the calculation of the assigned value:

i) non numerical results i.e. qualitative or semi-quantitative results,

ii) results reported as approximately 10, 100 or 1000 × greater or smaller than the majority of submitted results (as these were considered to be reporting errors),

iii) results where no percentage recovery was reported,

iv) results whose recovery was outside the range 60-140% [6],

v) results where no limit of quantification was reported.

For carbendazim, cyprodinil, pp-DDD (TDE), endosulfan sulfate, fenbuconazole, pyrimethanil, tebuconazole and tetraconazole, this procedure was straightforward and the robust mean was chosen as the assigned value.

There are several participants which have reported results for op'DDT. Expert advice was taken and these results may be a co-elute issue with pp'DDD and/or a misidentification of the residue. See Table 4 for additional pesticides reported by participants.

The assigned values for all analytes are shown in Table 6.

4.2. Standard Deviation for Proficiency, σ_p

The standard deviation for proficiency, σ_p, was set at a value that reflects best practice for the analyses in question.

For carbendazim, cyprodinil, pp-DDD (TDE), endosulfan sulfate, fenbuconazole, pyrimethanil, tebuconazole and tetraconazole, σ_p was derived from the appropriate form of the Horwitz equation [7].

The values for σ_p used to calculate z-scores from the reported results of this test are given in Table 6.

4.3. Individual z-Scores

Participants' z-scores were calculated as:

$$z = \frac{(x - x_a)}{\sigma_p}$$

where x = the participant's reported result,
x_a = the assigned value
and σ_p = the standard deviation for proficiency.

Participants' z-scores for all analytes are given in Table 1-Table 3 and shown as histograms in Figures 1–8. It is possible for the z-scores published in this report to differ slightly from the z-score that can be calculated using the formula given above. These differences arise from the necessary rounding of the actual assigned values and standard deviations for proficiency prior to their publication in Table 6.

The number and percentage of z-scores in the range $-2 \leq z \leq 2$ for all analytes are given in Table 7.

5. INTERPRETATION OF SCORES

In normal circumstances, over time, about 95% of z-scores will lie in the range $-2 \leq z \leq 2$. Occasional scores in the range $2 < |z| < 3$ are to be expected, at a rate of 1 in 20. Whether or not such scores are of importance can only be decided by considering them in the context of the other scores obtained by that laboratory.

Scores where $|z| > 3$ are to be expected at a rate of about 1 in 300. Given this rarity, such z-scores very strongly indicate that the result is not fit-for-purpose and almost certainly requires investigation.

The consideration of a set or sequence of z-scores over time provides more useful information than a single z-score. Examples of suitable methods of comparison are provided in the IUPAC International Harmonised Protocol for the Proficiency Testing of Analytical Chemistry Laboratories [5].

6. REFERENCES

1 Adobe Certified Document Services, http://www.adobe.com/misc/pki/cds_cp.html, accessed 12/05/2016.

2 ISO/IEC 17043:2010, Conformity assessment – General requirements for proficiency testing.

3 Fapas®, 2016, Protocol for Proficiency Testing Schemes, Part 1 – Common Principles, Version 5, Issued September 2016.

4 Fapas®, 2016, Protocol for Proficiency Testing Schemes, Part 2 – Fapas® – Food Chemistry Version 4, Issued September 2016.

5 Thompson, M., Ellison, S.L.R. and Wood, R., 2006, The International Harmonised Protocol for the Proficiency Testing of Analytical Chemistry Laboratories, *Pure Appl. Chem.*, **78**, No. 1, 145–196.

6 Guidance Document on Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis in Food and Feed, Document No. SANTE/11945/2015.

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

Table 1: Results and z-Scores for Carbendazim, Cyprodinil and pp-DDD (TDE)

laboratory number	analyte											
	carbendazim assigned value 66.0 µg/kg				cyprodinil assigned value 34.0 µg/kg				pp-DDD (TDE) assigned value 104 µg/kg			
	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score
001	86.5		10	1.4	34.0		10	0.0	145		10	1.8
002	68	79	10	0.1	32	102	10	-0.3	69	100	10	-1.5
003	76.0	80.9	5	0.7	36.2	72.4	5	0.3	#			
004	56.8	92.7	10	-0.6	34.1	105.1	10	0.0	109.1	101.6	10	0.2
005	58	79	1	-0.6	27	68	6	-0.9	90	86	6	-0.6
006	#				21.63	110.3	10	-1.7	#			
007	55.5	99	10	-0.7	24	82	10	-1.3	#			
008	47.9	88	10	-1.2	37.4	105	10	0.5	#			
009	#				28	100	10	-0.8	#			
010	#				#				#			
011	49.8		0.01	-1.1	44.0		0.01	1.3	108.0		0.01	0.2
012	50	79	10	-1.1	26	85	10	-1.1	93	90	10	-0.5
013	57	80	10	-0.6	37.2	90	10	0.4	103	83	10	-0.1
014	108		10	**2.9**	25		10	-1.2	110		10	0.3
015	#				#				#			

= not analysed LoQ = limit of quantification z-scores outside |z| >2 are shown in **bold,** see Section 5

Table 1 (continued): Results and z-Scores for Carbendazim, Cyprodinil and pp-DDD (TDE)

laboratory number	analyte											
	carbendazim assigned value 66.0 µg/kg				cyprodinil assigned value 34.0 µg/kg				pp-DDD (TDE) assigned value 104 µg/kg			
	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score
016	66	94	10	0.0	36	101	10	0.3	see comments			
017	62	80	10	-0.3	26	56	10	-1.1	#			
018	80	70	10	1.0	30	98	10	-0.5	#			
019	#				34	70-120	10	0.0	#			
020	#				37.7	90.4	5	0.5	#			
021	142		10	**5.2**	30.8		10	-0.4	120		10	0.7
022	125	113	10	**4.1**	49	115	10	2.0	168	100	10	**2.8**
023	59	90	10	-0.5	35	70	10	0.1	86	90	10	-0.8
024	75.0	78.2	1.0	0.6	#				96.0	86.4	10.0	-0.4
025	0			**-4.5**	35.60	100.07	0.01	0.2	0			**-4.5**
026	#				#				39.6	98	0.1	**-2.8**
027	19.20	30	10	**-3.2**	47.50	159	10	1.8	125.70	149	10	0.9
028	39	105	30	-1.9	<30	91	30		0		30	**-4.5**
029	#				38.9	106	5	0.7	140	100	5	1.6
030	#				#				#			

= not analysed LoQ = limit of quantification z-scores outside |z| >2 are shown in **bold,** see Section 5 see comments = table 5

Table 1 (continued): Results and z-Scores for Carbendazim, Cyprodinil and pp-DDD (TDE)

laboratory number	analyte											
	carbendazim assigned value 66.0 µg/kg				cyprodinil assigned value 34.0 µg/kg				pp-DDD (TDE) assigned value 104 µg/kg			
	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score
031	115.9	100	10	**3.4**	35.99	102	10	0.3	0			**-4.5**
032	60	89	10	-0.4	35	97	10	0.1	120	94	10	0.7
033	67		10	0.1	32		10	-0.3	97		10	-0.3
034	#				28		10	-0.8	98		10	-0.3
035	36.15	102	10	**-2.1**	25.21	95	10	-1.2	94.49	86	10	-0.4
036	86.0	100	10	1.4	83.5	100	10	**6.6**	see comments			
037	58.55		10	-0.5	28.06		10	-0.8	109.4		10	0.2
038	#				#				90.3		10	-0.6
039	68	96	5	0.1	34	102	5	0.0	#			
040	28			**-2.6**	37			0.4	#			
041	98.87	87.56	10	**2.3**	32.37	92.68	10	-0.2	#			
042	79		10	0.9	33		10	-0.1	#			
043	43.2	71	10.0	-1.6	30.7	88	10.0	-0.4	59.6	115	10.0	-1.9
044	65	106	10	-0.1	33	87	10	-0.1	125	84	10	0.9
045	64	84	10	-0.1	58	93	10	**3.2**	161	103	10	**2.5**

= not analysed LoQ = limit of quantification z-scores outside |z| >2 are shown in **bold,** see Section 5 see comments = table 5

Table 1 (continued): Results and z-Scores for Carbendazim, Cyprodinil and pp-DDD (TDE)

laboratory number	analyte											
	carbendazim assigned value 66.0 µg/kg				cyprodinil assigned value 34.0 µg/kg				pp-DDD (TDE) assigned value 104 µg/kg			
	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score
046	73	82.2	10	0.5	38	94.0	10	0.5	132	82.3	10	1.2
047	#				48	98	3	1.9	135	96	8	1.3
048	58	87	10	-0.6	34	129	10	0.0	#			
049	81.5	95	10	1.1	22.8	107	10	-1.5	48.2	129	10	**-2.4**
050	25	10	10	**-2.8**	38	10	10	0.5	see comments			
051	130	98	10	**4.4**	25	96	10	-1.2	210	97	10	**4.6**
052	52.00	70	10	-1.0	31.00	90	10	-0.4	59.69	90	10	-1.9
053	69	95	5	0.2	36	108	5	0.3	90	75	5	-0.6
054	#				66	90	10	**4.3**	#			

= not analysed LoQ = limit of quantification z-scores outside |z| >2 are shown in **bold,** see Section 5 see comments = table 5

Table 2: Results and z-Scores for Endosulfan Sulfate, Fenbuconazole and Pyrimethanil

laboratory number	analyte											
	endosulfan sulfate assigned value 157 µg/kg				fenbuconazole assigned value 228 µg/kg				pyrimethanil assigned value 76.0 µg/kg			
	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score
001	249		10	**2.8**	210		10	-0.4	73.0		10	-0.2
002	205	105	10	1.5	221	90	10	-0.1	81	95	10	0.3
003	#				155.4	86.4	5	-1.6	97.6	94.8	5	1.3
004	174.7	114.7	10	0.5	248.3	112.1	10	0.5	75.9	107.7	10	0.0
005	127	75	9	-0.9	130	66	12	**-2.1**	61	71	2.4	-0.9
006	140.7	92.35	10	-0.5	149.4	106.4	10	-1.7	46.27	121.9	10	-1.8
007	131	82	10	-0.8	238	93	10	0.2	59	118	10	-1.0
008	208.0	92	10	1.5	221.2	110	10	-0.1	84.3	116	10	0.5
009	#				286	100	5	1.3	29	100	10	**-2.8**
010	150	90	20	-0.2	#				65	85	10	-0.7
011	166.0		0.01	0.3	164.0		0.01	-1.4	87.0		0.01	0.7
012	140	95	10	-0.5	210	105	10	-0.4	68	81	10	-0.5
013	191.7	70	10	1.1	252.7	90	10	0.6	78.1	100	10	0.1
014	159		10	0.1	210		10	-0.4	57		10	-1.1
015	156.5	95.86	20	0.0	#				#			

= not analysed LoQ = limit of quantification z-scores outside |z| >2 are shown in **bold,** see Section 5

Table 2 (continued): Results and z-Scores for Endosulfan Sulfate, Fenbuconazole and Pyrimethanil

laboratory number	analyte											
	endosulfan sulfate assigned value 157 µg/kg				fenbuconazole assigned value 228 µg/kg				pyrimethanil assigned value 76.0 µg/kg			
	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score
016	159	85	10	0.1	294	104	10	1.5	84	102	10	0.5
017	226	108	10	**2.1**	272	112	10	1.0	70	92	10	-0.4
018	100	79	10	-1.7	230	102	10	0.1	80	84	100	0.2
019	#				230	70-120	10	0.1	71	70-120	10	-0.3
020	266.5	101.8	5	**3.3**	#				100.8	101.8	5	1.5
021	180		10	0.7	206		10	-0.5	72.4		10	-0.2
022	#				279	109	10	1.1	94	115	10	1.1
023	152	100	10	-0.1	238	120	10	0.2	85	80	10	0.5
024	0		10	**-4.7**	#				65.4	76.7	5.0	-0.6
025	101.38	98.34	0.01	-1.7	127.6	81.43	0.01	**-2.2**	76.8	82.79	0.01	0.0
026	42.9	96	0.1	**-3.4**	#				#			
027	187.80	124	10	0.9	205.00	146	10	-0.5	101.90	189	10	1.5
028	182	123	30	0.8	183	76	30	-1.0	55	78	30	-1.3
029	168	98	5	0.3	205	100	5	-0.5	85.5	97	5	0.6
030	#				#				#			

= not analysed LoQ = limit of quantification z-scores outside |z| >2 are shown in **bold,** see Section 5

Table 2 (continued): Results and z-Scores for Endosulfan Sulfate, Fenbuconazole and Pyrimethanil

laboratory number	analyte											
	endosulfan sulfate assigned value 157 µg/kg				fenbuconazole assigned value 228 µg/kg				pyrimethanil assigned value 76.0 µg/kg			
	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score
031	197.72	94	10	1.2	270.22	104	10	0.9	76.72	102	10	0.0
032	157	104	10	0.0	211	97	10	-0.4	77	97	10	0.1
033	92		2	-2.0	182		10	-1.0	70		10	-0.4
034	#				#				0		10	**-4.5**
035	0			**-4.7**	176.47	110	10	-1.1	68.81	107	10	-0.4
036	157.8	100	10	0.0	286.2	100	10	1.3	76.2	100	10	0.0
037	165.83		10	0.3	157.75		10	-1.5	69.12		10	-0.4
038	#				173		10	-1.2	65		10	-0.7
039	184	107	5	0.8	238	104	5	0.2	77	114	5	0.1
040	#				312			1.9	92			1.0
041	#				#				#			
042	199		10	1.3	288		10	1.3	85		10	0.5
043	104.5	106	10.0	-1.6	182	78	10.0	-1.0	55.8	105	10.0	-1.2
044	176	115	10	0.6	218	91	10	-0.2	79	107	10	0.2
045	142	97	10	-0.4	260	87	10	0.7	137	86	10	**3.6**

= not analysed LoQ = limit of quantification z-scores outside |z| >2 are shown in **bold,** see Section 5

Table 2 (continued): Results and z-Scores for Endosulfan Sulfate, Fenbuconazole and Pyrimethanil

laboratory number	analyte											
	endosulfan sulfate assigned value 157 µg/kg				fenbuconazole assigned value 228 µg/kg				pyrimethanil assigned value 76.0 µg/kg			
	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score
046	172	97.2	10	0.5	260	111	10	0.7	80	91.9	10	0.2
047	#				239	82	60	0.2	115	96	2	**2.3**
048	194	122	10	1.1	249	115	10	0.5	79	121	10	0.2
049	82.8	131	10	**-2.2**	201	101	10	-0.6	63.7	107	10	-0.7
050	15	10	2	**-4.3**	260	10	10	0.7	68	10	10	-0.5
051	80	97	10	**-2.3**	0			**-5.0**	68	98	10	-0.5
052	192.50	80	10	1.1	204.00	90	10	-0.5	73.00	90	10	-0.2
053	163	75	5	0.2	208	105	5	-0.4	81	96	5	0.3
054	100	73	10	-1.7	470	88	10	**5.3**	104	93	10	1.7

= not analysed LoQ = limit of quantification z-scores outside |z| >2 are shown in **bold,** see Section 5

Table 3: Results and z-Scores for Tebuconazole and Tetraconazole

laboratory number	analyte							
	tebuconazole assigned value 87.1 µg/kg				tetraconazole assigned value 130 µg/kg			
	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score
001	99.8		10	0.7	157		10	1.0
002	103	110	10	0.8	110	74	10	-0.7
003	91.2	72.3	5	0.2	145.4	82.0	5	0.5
004	87.7	112.4	10	0.0	#			
005	65	81	12	-1.2	116	69	6	-0.5
006	58.50	102.4	10	-1.5	91.53	109.9	10	-1.4
007	93.7	87	10	0.3	116	90	10	-0.5
008	88.9	88	10	0.1	134.2	95	10	0.2
009	79	100	10	-0.4	#			
010	#				#			
011	111.0		0.01	1.2	109		0.01	-0.7
012	78	96	10	-0.5	120	97	10	-0.4
013	91.1	100	10	0.2	154	90	10	0.9
014	78		10	-0.5	114		10	-0.6
015	#				#			

= not analysed LoQ = limit of quantification

Table 3 (continued): Results and z-Scores for Tebuconazole and Tetraconazole

laboratory number	analyte							
	tebuconazole assigned value 87.1 µg/kg				tetraconazole assigned value 130 µg/kg			
	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score
016	93	96	10	0.3	146	97	10	0.6
017	80	76	10	-0.4	130	108	10	0.0
018	70	77	10	-0.9	90	85	10	-1.4
019	87	70-120	10	0.0	140	70-120	10	0.4
020	177.9	99.4	5	**4.7**	197.7	101.2	5	**2.4**
021	70.7		10	-0.9	135		10	0.2
022	109	106	10	1.1	149	110	10	0.7
023	100	90	10	0.7	154	100	10	0.9
024	#				#			
025	68.65	89.27	0.01	-1.0	27.60	113.08	0.01	**-3.6**
026	#				#			
027	67.20	71	10	-1.0	108.3	104	10	-0.8
028	108	84	30	1.1	1409	82	30	**45.3**
029	84.6	100	5	-0.1	91.8	104	5	-1.3
030	#				#			

= not analysed LoQ = limit of quantification z-scores outside |z| >2 are shown in **bold,** see Section 5

Table 3 (continued): Results and z-Scores for Tebuconazole and Tetraconazole

laboratory number	analyte							
	tebuconazole assigned value 87.1 µg/kg				tetraconazole assigned value 130 µg/kg			
	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score
031	100.72	103	10	0.7	159.08	104	10	1.0
032	83	102	10	-0.2	110	101	10	-0.7
033	88		10	0.0	91		10	-1.4
034	73		10	-0.7	#			
035	84.48	92	10	-0.1	117.62	89	10	-0.4
036	98.8	100	10	0.6	166.5	100	10	1.3
037	64.92		10	-1.2	99.72			-1.1
038	108		10	1.1	108		10	-0.8
039	91	109	5	0.2	139	98	5	0.3
040	124			1.9	#			
041	118.07	93.97	10	1.6	#			
042	90		10	0.2	138		10	0.3
043	73.6	92	10.0	-0.7	121.5	119	10.0	-0.3
044	83	79	10	-0.2	123	104	10	-0.2
045	105	106	10	0.9	180	92	10	1.8

= not analysed LoQ = limit of quantification

Table 3 (continued): Results and z-Scores for Tebuconazole and Tetraconazole

laboratory number	analyte							
	tebuconazole assigned value 87.1 µg/kg				tetraconazole assigned value 130 µg/kg			
	result µg/kg	recovery %	LoQ µg/kg	z-score	result µg/kg	recovery %	LoQ µg/kg	z-score
046	96	107	10	0.5	141	107	10	0.4
047	124	107	4	1.9	#			
048	70	107	10	-0.9	150	116	10	0.7
049	61.9	110	10	-1.3	80.7	110	10	-1.7
050	250	10	10	**8.5**	156	10	10	0.9
051	55	96	10	-1.7	100	103	10	-1.1
052	80.00	120	10	-0.4	153.00	100	10	0.8
053	75	107	5	-0.6	114	106	5	-0.6
054	100	96	10	0.7	305	79	10	**6.2**

= not analysed LoQ = limit of quantification z-scores outside |z| >2 are shown in **bold,** see Section 5

Table 4: Additional Pesticide Residues Reported

laboratory number	pesticide residue >15 µg/kg	result µg/kg	recovery %	LoQ µg/kg
002	Bitertanol	30	83	10
002	op'-DDT	65	100	10
013	op'-DDT	204	74	10
023	op'-DDT	86	90	10
028	op'-DDT	94	77	30
036	op'-DDT	141.3	100	10
042	op'-DDT	150		10
050	op'-DDT	211	10	10
052	pp'-DDT	118.45	90	10

Table 5: Participants' Comments

participant number	comments
002	The LOQ for most of Analytes tested for but not detected is 10 µg/kg.
008	Spinosad was also detected at the same approx. concentration 6.4?g/kg (semiquantitative, as it is between LOD and LOQ), in the blank sample provided by FAPAS
016	We have detected as a sum p,p´-DDT+o,p-DDT, with 140 µg/kg as result and 96 % Recovery. Our limit of quantification is 10 µg/kg as sum
018	We have positive results for the sum DDD-P,P + DDT-O,P = 110 µg/Kg (%recovery: 84%)
023	pp'-DDD (TDE)+op'-DDT= 86 µg/kg
027	Recovery samples were spiked in peach pure.
032	Spinosad has been detected below the LoQ (10ug/kg)
036	op'-DDT result is the op'-DDT + pp'-DDD
037	DDD p,p' + DDT p,p' sum 109.4 ug/kg
044	Blank with Spinosad < LoQ
045	We also found traces of Spinosad (7 µg/kg)
050	our laboratory reported o,p DDT pesticide including p,p DDD pesticide . because of short run time for GC method their retention times and all ions are the same.
053	traces of alpha-Endosulfan and beta-Endosulfan < 5 µg/kg
054	Additionally compounds have been found with the dichlorodiphenyl group

comments are as submitted by participants

Table 6: Assigned Values and Standard Deviations for Proficiency

analyte	data points, *n*	assigned value, x_a, µg/kg	uncertainty, *u*	standard deviation for proficiency, σ_p, µg/kg	
carbendazim	30	66.0	3.26	Horwitz [7]	14.5
cyprodinil	35	34.0	1.21	Horwitz [7]	7.48
pp-DDD (TDE)	21	104	9.37	Horwitz [7]	22.9
endosulfan sulfate	34	157	7.63	Horwitz [7]	33.2
fenbuconazole	34	228	8.00	Horwitz [7]	45.5
pyrimethanil	37	76.0	2.44	Horwitz [7]	16.7
tebuconazole	38	87.1	2.85	Horwitz [7]	19.2
tetraconazole	33	130	5.41	Horwitz [7]	28.3

Table 7: Number and Percentage of z-Scores where |z| ≤2

analyte	number of scores where |z| ≤2	total number of scores	% |z| ≤2
carbendazim	30	41	73
cyprodinil	44	47	94
pp-DDD (TDE)	25	33	76
endosulfan sulfate	35	44	80
fenbuconazole	42	46	91
pyrimethanil	46	50	92
tebuconazole	47	49	96
tetraconazole	39	43	91

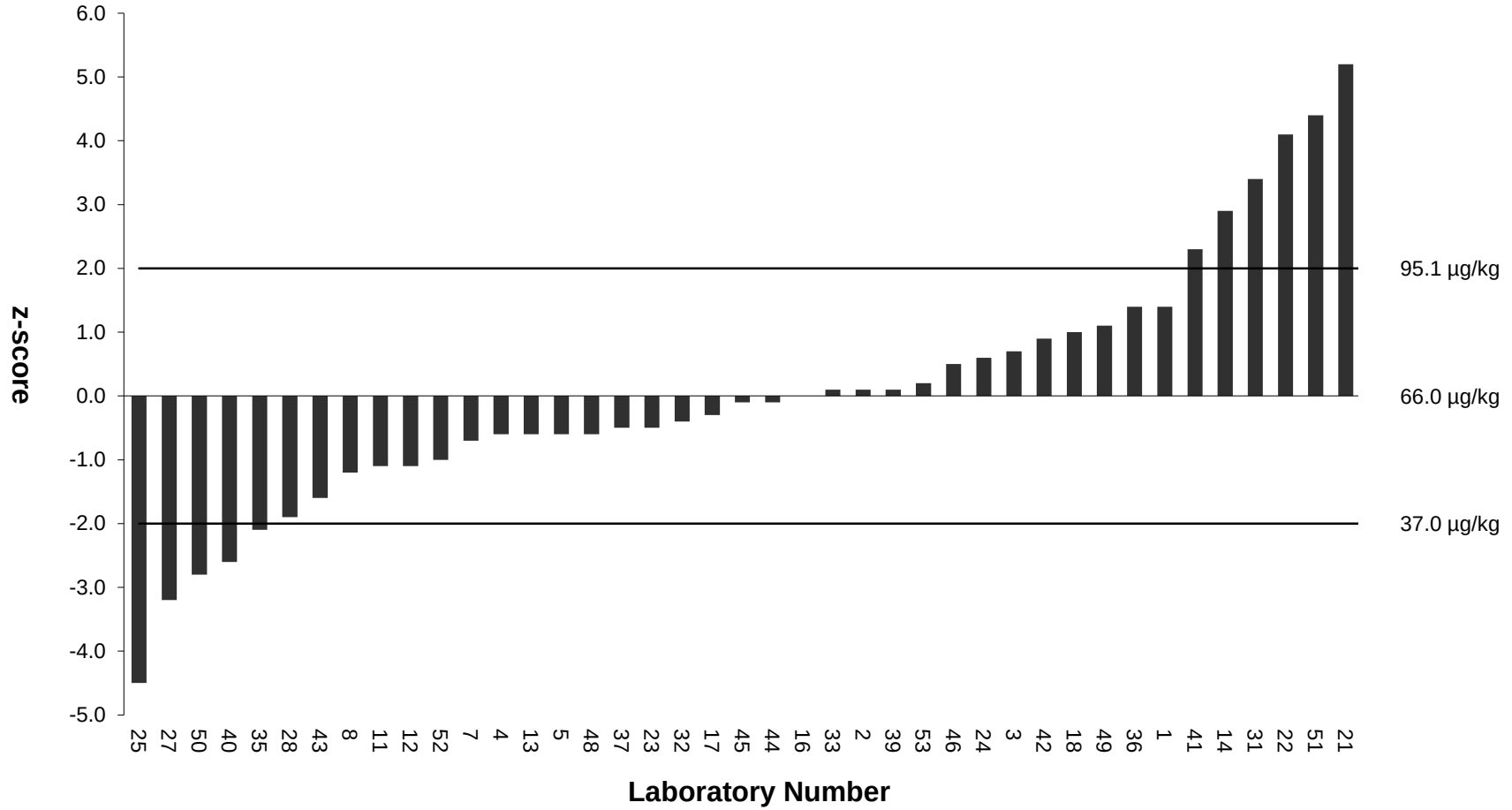

Figure 1: z-Scores for Carbendazim

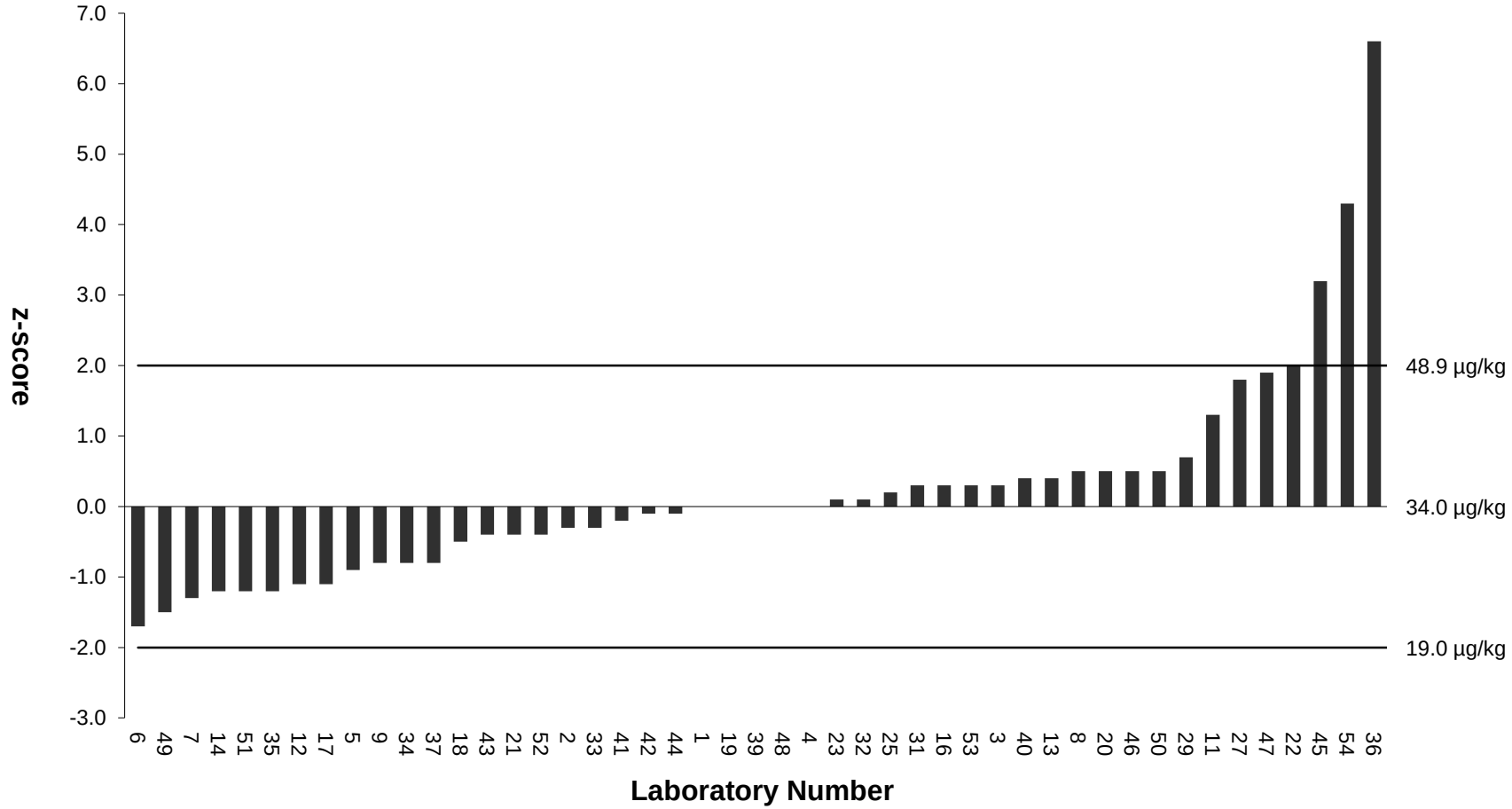

Figure 2: z-Scores for Cyprodinil

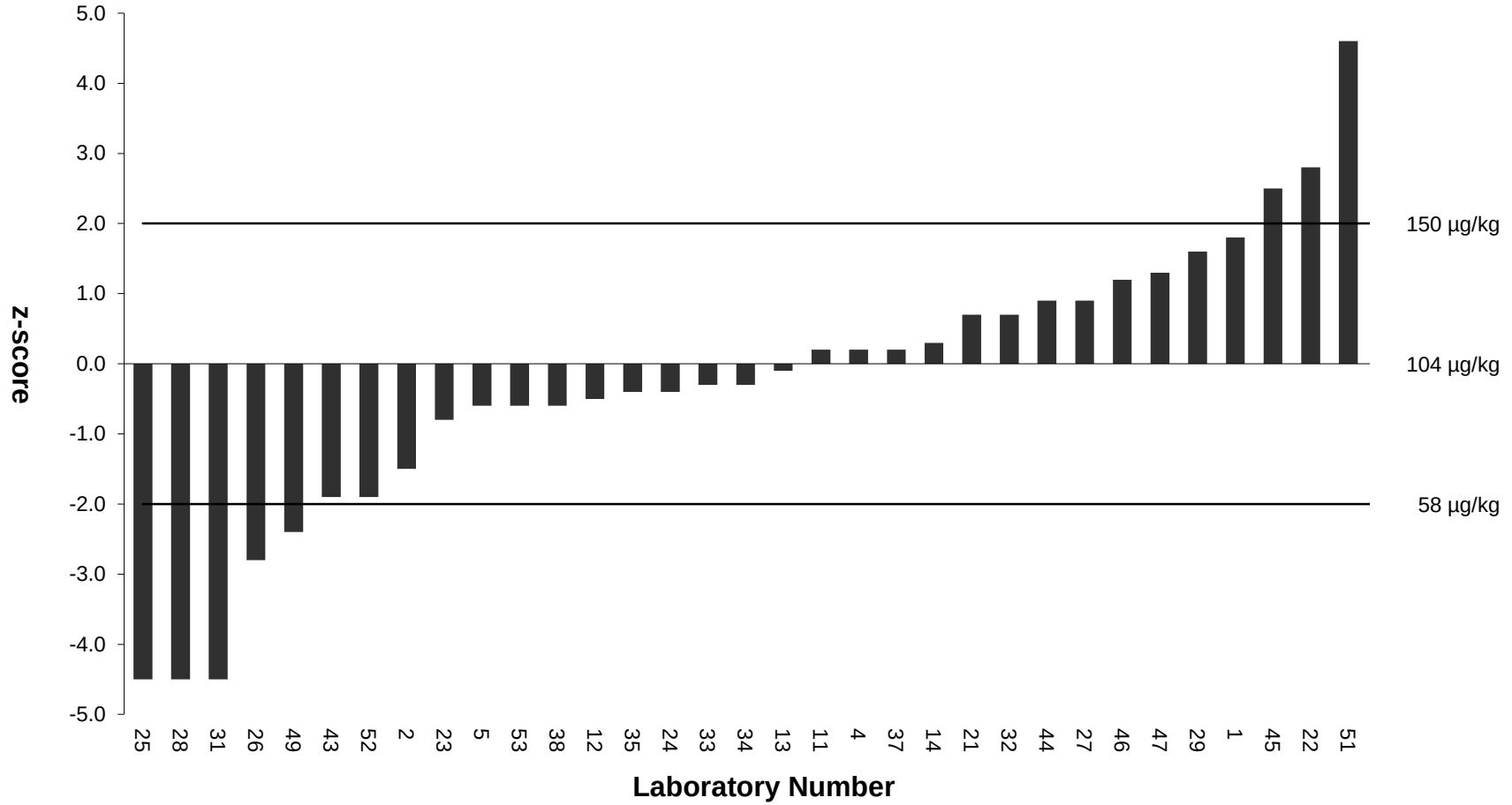

Figure 3: z-Scores for pp-DDD (TDE)

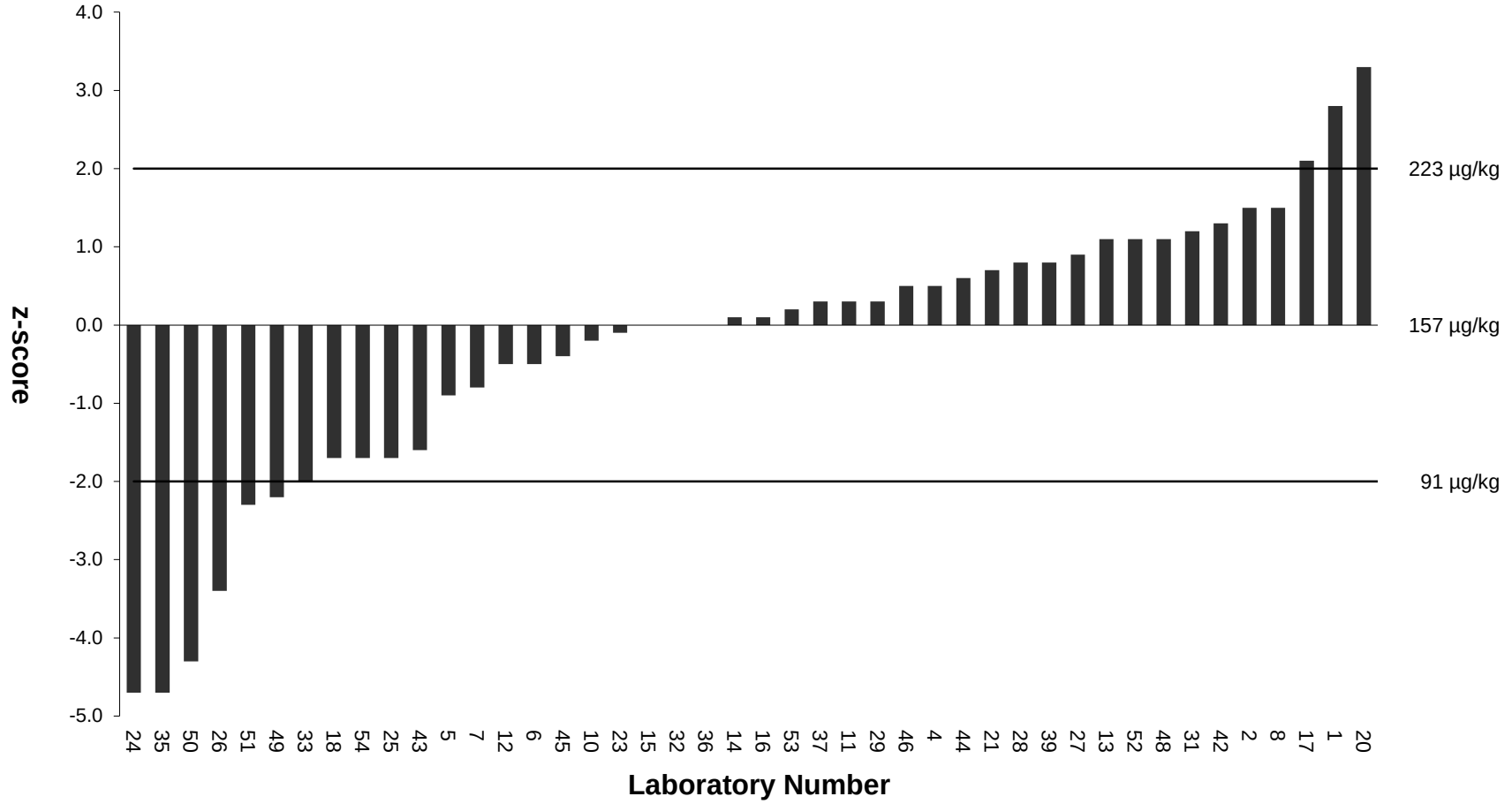

Figure 4: z-Scores for Endosulfan Sulfate

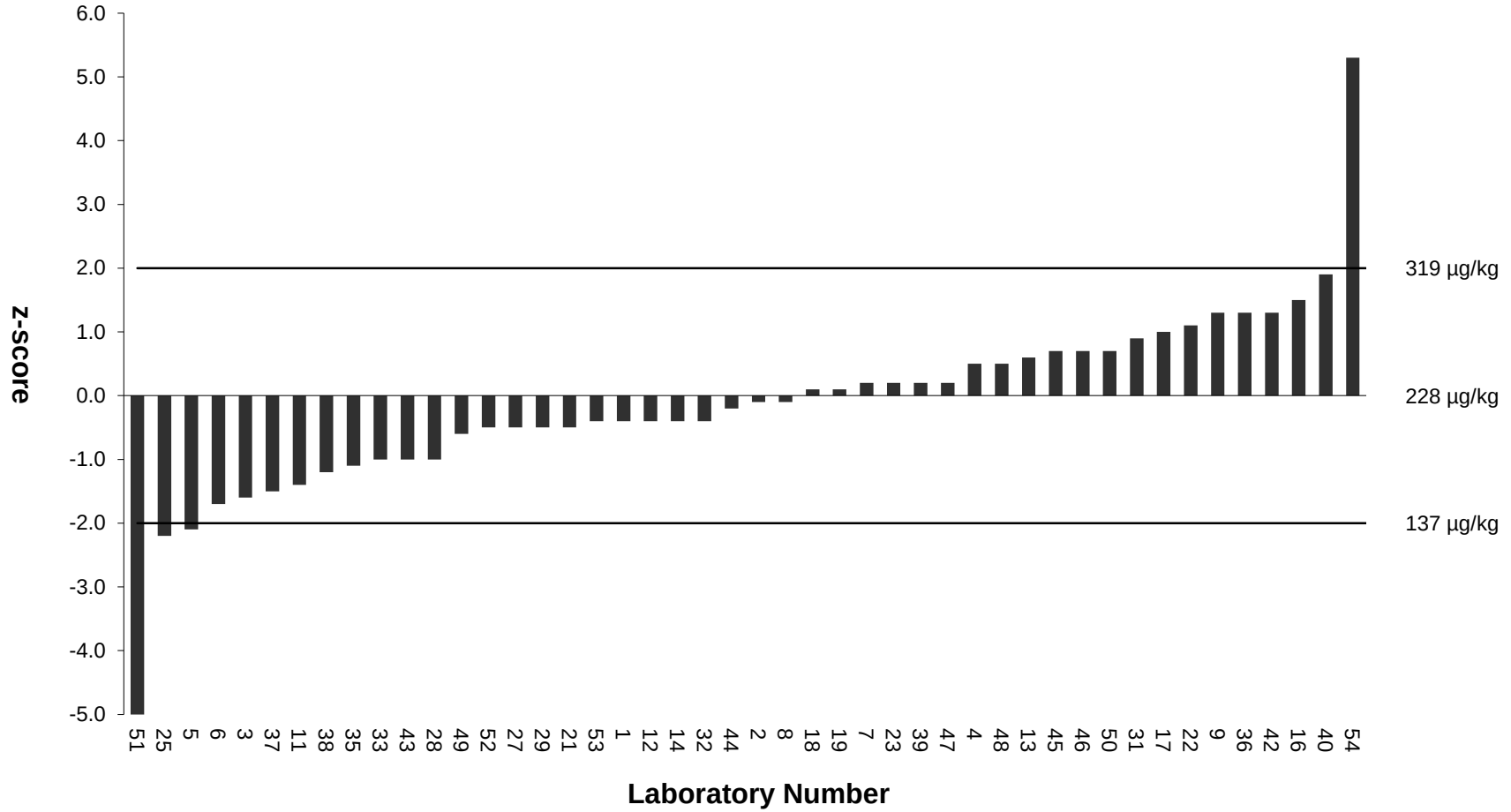

Figure 5: z-Scores for Fenbuconazole

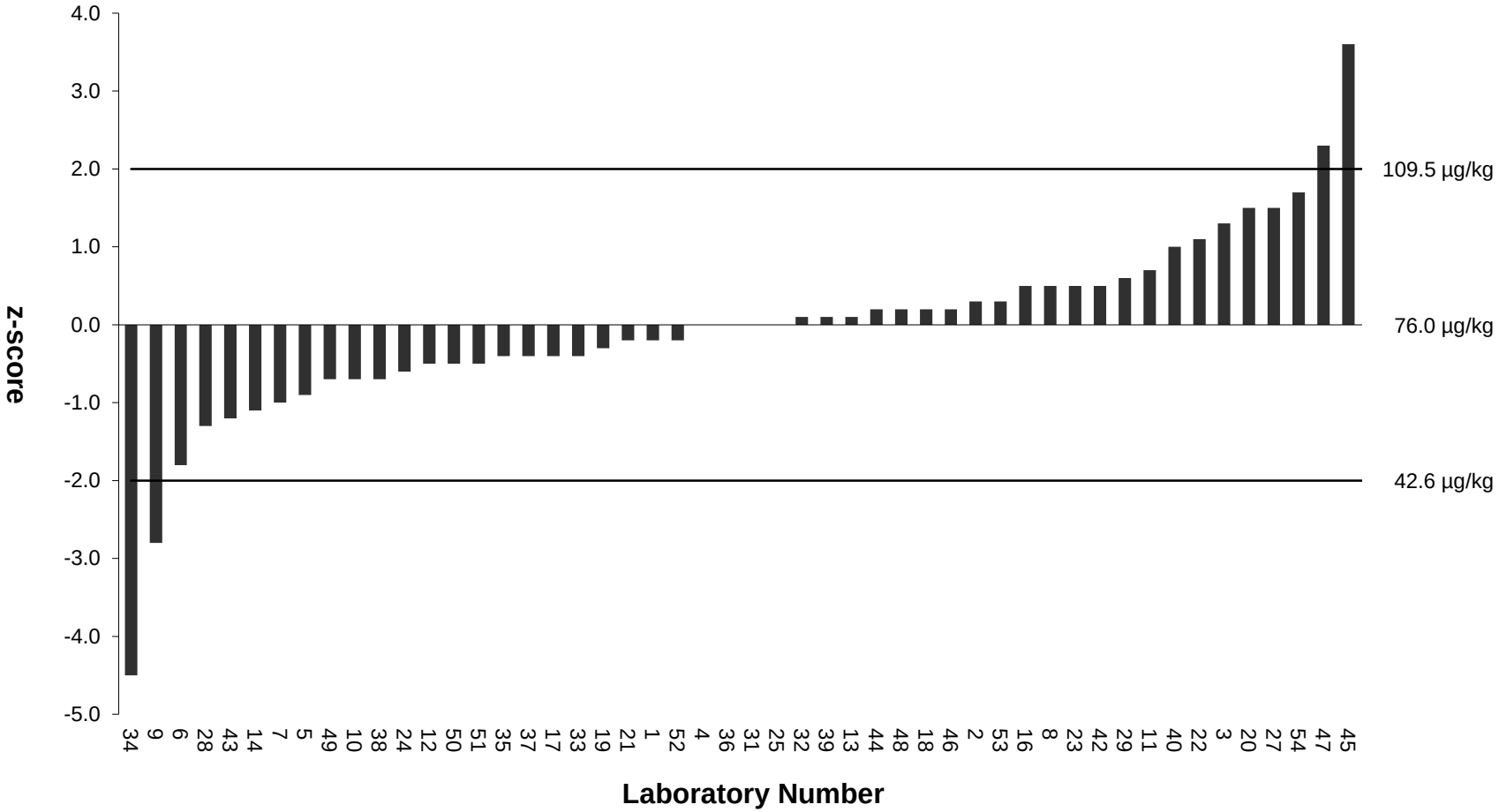

Figure 6: z-Scores for Pyrimethanil

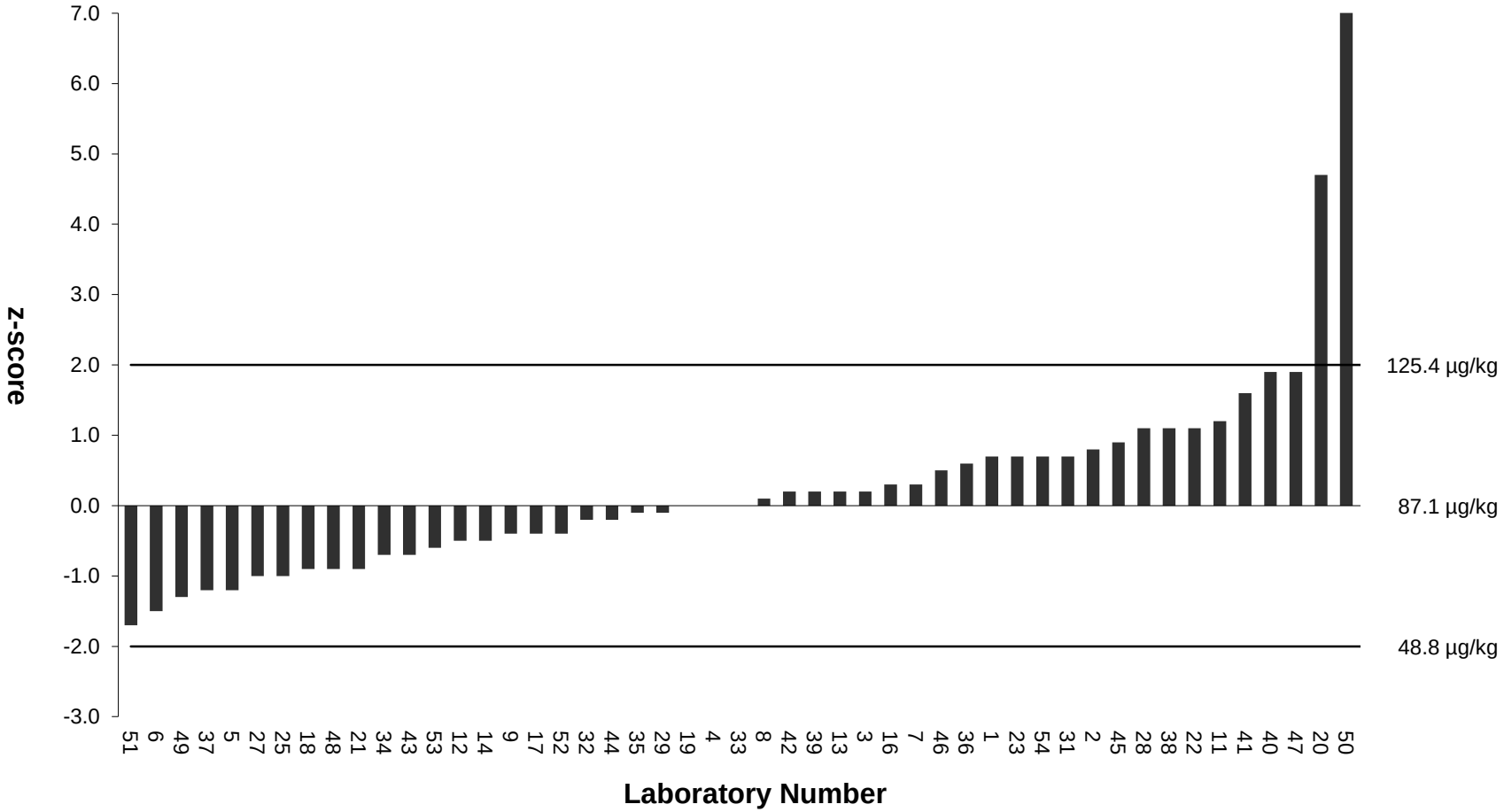

Figure 7: z-Scores for Tebuconazole

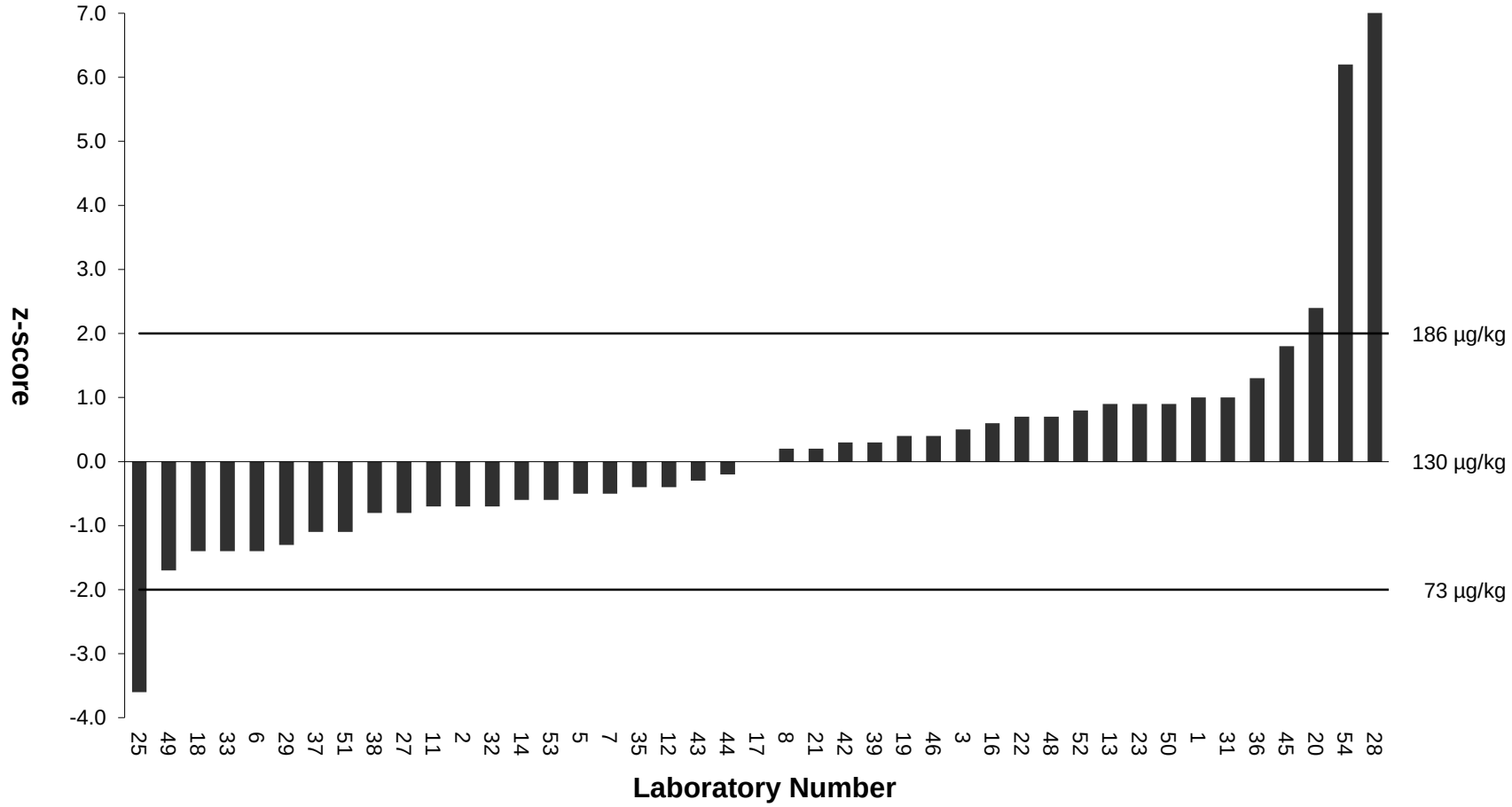

Figure 8: z-Scores for Tetraconazole

APPENDIX I: Analytical Methods Used by Participants

Methods are tabulated according to the information supplied by participants, but some responses may have been combined or edited for clarity.

Accredited Method Used	laboratory number
yes	001 003 004 005 006 008 010 011 012 013 014 016 017 018 024 027 029 030 031 032 034 035 037 039 042 043 044 045 046 049 050 051 053 054
no	002 009 026 048

Method Based On	laboratory number
International Standard	002 004 008 009 010 012 013 014 016 017 018 022 026 027 029 031 032 034 044 045 046 050 051 053 054
National Standard	030
Paper Published In An International Journal	006 048 049
Manufacturer/Kit Instructions/Technical Note	042
In house method	001 003 005 011 024 035 037 039 043

Quoted percentage recovery measured in same analytical batch as test material	laboratory number
yes	001 002 004 005 006 008 010 012 013 017 018 022 024 026 027 029 030 031 034 035 039 042 043 044 045 046 048 049 050 053 054
no	003 009 014 016 032 037 051

If measured in this batch, stage spike added	laboratory number
prior to extraction	001 002 004 005 006 008 010 011 012 013 016 017 018 022 024 026 027 029 030 031 034 035 039 042 043 044 045 046 048 049 051 053 054
prior to clean up	050

Concentration of Spike (µg/kg)	laboratory number
≥1 - <5	012
≥5 - <10	039
≥10 - <25	005 006 017 022 027 029 032 042 043 048 049
≥50 - <100	001 003 010 016 018 030 031 035 044 046 050 051 053
≥100	002 004 008 013 024 026 034 045

Composition of Blank Commodity used for Spiking	laboratory number
blank provided	001 004 005 008 010 012 013 016 017 018 024 026 029 030 031 034 037 039 042 044 045 046 048 049 050 051
19213b	009
Bio Nectarine	032
in-house blank	002 006
peach	054
Peach pure	027

Calibration	laboratory number
standard addition	014 018
matrix-matched	001 003 004 006 009 012 022 027 030 031 032 034 039 042 045 046 049 050 051 053 054
solvent	026
multi-level	001 002 004 005 006 010 011 013 016 017 024 027 029 037 043 044 048 049
single-level	008 035

Internal Standard Added	laboratory number
yes	001 002 004 005 009 011 013 014 016 017 018 027 029 030 032 035 037 042 043 044 045 046 051 053 054
no	003 006 008 010 012 022 024 026 031 034 039 048 049 050

Internal Standard Used	laboratory number
Chlorpyrifos deuterated	027
Fluorene D10	035
Heptachlor-epxide	030
multi internal standards	002
p/terphenyol D14, D4 Imidacloprid	011
PCB, TTP	045
Sulfotep/PCB 31	032
TCPP	029
TDCPP	014
TPM(triphenyl methane) GC, Atrazine-d5 LC	005
TPP	001 004 009 013 016 017 018 037 042 043 051 053 054
Sulprofos	018
PCB	054
Malathion D6, Chlorpyrifos methyl D6, Atrazine D5, Diflufenican D3, Imidaclorprid D4,	037
Tetrachloronaphthaline	053
SULPROFOS	017

GC Method: Sample Weight (g)	laboratory number
≥5 - <10	002 010 014 026 027 035 044 051
≥10 - <20	001 003 004 005 006 008 009 011 012 013 016 017 018 022 024 029 030 031 032 034 037 039 042 043 045 046 048 049 050 053 054

GC Method: Extraction Solvent Components	laboratory number
acetone	039 045 050 053
acetonitrile	001 002 003 004 005 008 009 010 012 013 014 016 017 018 022 024 026 027 029 030 031 032 034 035 042 043 044 046 049 051 054
ethyl acetate	006 011 037

GC Method: Extraction Solvent Components (continued)	laboratory number
acetic acid	009 048
dichloromethane, petroleum ether	039
hexane	053
Isooctan	045

GC Method: Extraction pH Adjusted	laboratory number
yes	001 002 008 012 016 027 035 037 043 044 046 050 054
no	003 004 005 006 009 010 011 013 014 017 018 022 024 026 029 030 031 032 034 039 042 045 048 049 051 053

GC Method: Extraction Techniques Used	laboratory number
macerate at room temperature	011
QuEChERS	001 002 003 004 005 008 009 010 012 013 014 016 017 018 022 024 027 029 031 032 034 035 042 043 044 045 046 048 049 050 051 054
liquid-liquid partition	006 026 030 037 039

GC Method: Sample Clean-up Technique	laboratory number
GPC/HPGPC	014 053
none	006 008 031 032 037 039 044 045
solid phase extraction (SPE) (column/cartridge)	010 011 030 050 053
solid phase extraction (SPE) (dispersive)	001 002 003 004 005 009 012 013 017 024 026 027 029 034 035 042 043 046 048 049 051 054
Quechers	018

GC Method: SPE Sorbent Type	laboratory number
PSA	001 002 003 004 005 008 010 012 013 014 017 027 029 032 034 035 042 043 046 048 049 050 051 054
NH2	031
Mixed Mode	024 026
Magnesium sulphate	017

GC Method: GC Column Packing	laboratory number
50% methyl 50% phenyl polysiloxane	016 024 050
95% methyl 5% phenyl polysiloxane	001 003 004 006 008 010 011 012 017 027 029 030 031 032 034 035 039 042 043 044 045 046 048 049 051 053 054
95% dimethyl polysiloxane 5% diphenyl	018
DB5-MS	037

GC Method: GC Detector Type	laboratory number
ECD	008 026 053
FPD	053
MS	003 005 010 011 024 030 034 045 050 051 053 054
MS-MS	001 002 004 006 009 012 013 014 016 017 018 022 027 029 032 035 037 039 042 043 044 046 048 049

LC Method: Sample Weight (g)	laboratory number
≥5 - <10	002 014 027 035 051 053
≥10 - <20	001 003 004 005 008 009 011 012 013 016 017 018 024 029 030 031 032 034 037 039 042 043 045 046 048 049 050 054

LC Method: Extraction Solvent Components	laboratory number
acetonitrile	001 002 003 004 005 008 009 012 013 014 016 017 018 022 024 027 029 030 031 032 034 035 037 042 043 044 045 046 049 050 051 053 054

LC Method: Extraction Solvent Components (continued)	laboratory number
ethyl acetate	011
methanol	001
1% Actic acid	009
acetone, dichloromethane, petroleum ether	039

LC Method: Extraction pH Adjusted	laboratory number
yes	001 002 008 012 016 027 035 037 043 044 046 050 054
no	003 004 005 009 011 013 014 017 018 022 024 029 030 031 032 034 039 042 045 048 049 051 053

LC Method: Extraction Techniques Used	laboratory number
macerate at room temperature	011
QuEChERS	001 002 003 004 005 008 009 012 013 014 016 017 018 022 024 027 029 031 032 034 035 042 043 044 045 046 048 049 050 051 053 054
liquid-liquid partition	030 037 039

LC Method: Sample Clean-up Technique	laboratory number
GPC/HPGPC	031
none	005 011 012 032 037 039 045
solid phase extraction (SPE) (column/cartridge)	014 017 030 050
solid phase extraction (SPE) (dispersive)	001 002 003 004 008 009 013 024 027 029 034 035 042 043 046 048 049 051 053 054
Quechers	018

LC Method: SPE Sorbent Type	laboratory number
C18	053

LC Method: SPE Sorbent Type (continued)	laboratory number
PSA	001 002 003 004 008 013 014 017 027 029 032 034 035 042 043 046 048 049 050 051 054
NH2	030 031
Mixed Mode	024
Magnesium sulphate	017

LC Method: HPLC Column Packing	laboratory number
C18	001 003 004 005 008 009 012 013 014 016 017 018 024 027 030 031 032 034 035 037 039 042 043 044 046 048 049 050 051 053 054
biphenylich	029

LC method: Mobile Phase Components	laboratory number
acetonitrile	003 024 031 044 045
ammonium acetate	049
ammonium formate	001 004 005 009 027 050 054
formic acid	009 027
methanol	001 002 003 004 005 009 013 014 018 027 029 032 035 037 039 042 049 051
water	001 003 004 008 009 012 013 016 017 018 027 034 035 037 039 042 043 044 045 046 048 049 053

LC Method: Detector Type	laboratory number
fluorescence	030
MS-MS	001 002 003 004 005 008 009 011 012 013 014 016 017 018 022 024 027 029 031 032 034 035 037 039 042 043 044 045 046 048 049 050 051 053 054

Carbendazim

Method Principle	laboratory number
LC	001 002 003 004 005 008 011 013 014 017 018 022 024 027 031 032 035 037 039 042 043 044 045 046 048 049 050 051 053

Identification by Mass Spectrometry	laboratory number
yes	001 003 004 005 008 011 013 014 017 018 022 024 027 031 032 035 037 039 042 043 044 045 046 048 049 050 051 053
no	002

Cyprodinil

Method Principle	laboratory number
GC	001 002 006 009 011 013 017 018 027 031 032 034 037 042 044 045 048 049 054
LC	003 004 005 008 014 022 035 039 043 046 050 051 053

Identification by Mass Spectrometry	laboratory number
yes	001 003 004 005 006 008 009 011 013 014 017 018 022 027 031 032 034 035 037 039 042 043 044 045 046 048 049 050 051 053 054
no	002

pp'-DDD (TDE)

Method Principle	laboratory number
GC	001 002 004 005 011 013 014 022 024 026 027 032 034 035 037 043 044 045 046 049 051 053

Identification by Mass Spectrometry	laboratory number
yes	001 004 005 011 013 014 022 024 027 032 034 035 037 043 044 045 046 049 051
no	002 026 053

Endosulfan Sulfate

Method Principle	laboratory number
GC	001 002 004 005 006 008 010 011 013 017 018 026 027 032 037 039 042 043 044 045 046 048 049 050 051 053 054
LC	014 031

Identification by Mass Spectrometry	laboratory number
yes	001 004 005 006 010 011 013 014 017 018 027 031 032 037 039 042 043 044 045 046 048 049 050 051 054
no	002 008 026 053

Fenbuconazole

Method Principle	laboratory number
GC	001 004 005 006 032 037 044 045 048 050 054
LC	002 003 008 009 011 013 014 017 018 022 027 031 035 039 042 043 046 049 053

Identification by Mass Spectrometry	laboratory number
yes	001 003 004 005 006 008 009 011 013 014 017 018 022 027 031 032 035 037 039 042 043 044 045 046 048 049 050 053 054
no	002

Pyrimethanil

Method Principle	laboratory number
GC	001 004 006 009 010 011 013 017 018 027 032 037 043 044 048 049 050 051
LC	002 003 005 008 014 022 024 031 035 039 042 045 046 053 054

Identification by Mass Spectrometry	laboratory number
yes	001 003 004 005 006 008 009 010 011 013 014 017 018 022 024 027 031 032 035 037 039 042 043 044 045 046 048 049 050 051 053 054
no	002

Tebuconazole

Method Principle	laboratory number
GC	002 004 005 006 009 011 013 017 018 032 035 037 042 043 044 045 048 049 054
LC	001 003 008 014 022 027 031 034 039 046 050 051 053

Identification by Mass Spectrometry	laboratory number
yes	001 003 004 005 006 008 009 011 013 014 017 018 022 027 031 032 034 035 037 039 042 043 044 045 046 048 049 050 051 053 054
no	002

Tetraconazole

Method Principle	laboratory number
GC	006 013 017 018 032 037 042 043 044 045 048 049
LC	001 002 003 005 008 011 014 022 027 031 035 039 046 050 051 053 054

Identification by Mass Spectrometry	laboratory number
yes	001 003 005 006 008 011 013 014 017 018 022 027 031 032 035 037 039 042 043 044 045 046 048 049 050 051 053 054
no	002

APPENDIX II: Fapas® SecureWeb, Protocol and Contact Details

1. Fapas® SECUREWEB

Access to the secure area of our website is only available to participants in our proficiency tests. Please contact us if you require a UserID and Password. Fapas® SecureWeb allows participants to:

- Obtain their laboratory numbers for the proficiency tests in which they have participated.
- View the results they submitted in past and current proficiency tests.
- Submit their results and methods for current tests.
- Review future tests they have ordered.
- Order proficiency tests, reference materials and quality control materials.
- Freely download copies of reports (PDF file), of proficiency tests in which they have participated.
- View charts of their z-scores obtained in previous Fapas® – Food Chemistry proficiency tests.

2. PROTOCOL

The Protocols [3, 4] set out how Fapas® – Food Chemistry is organised. Copies can be downloaded from our website.

3. CONTACT DETAILS

This report was prepared and authorised on behalf of Fapas® by Simon Hunter (Round Coordinator). Participants with any comments or concerns about this proficiency test should contact:

Fapas®

Fera Science Ltd (Fera)
National Agri-Food Innovation Campus
Sand Hutton
York
YO41 1LZ
UK

Tel: +44 (0)1904 462100
Fax: +44 (0)1904 500440

info@fapas.com

www.fapas.com