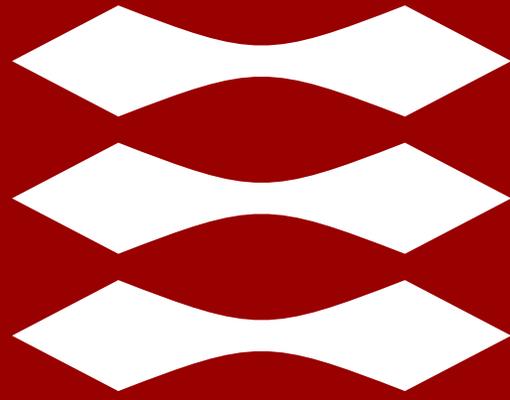


DTU

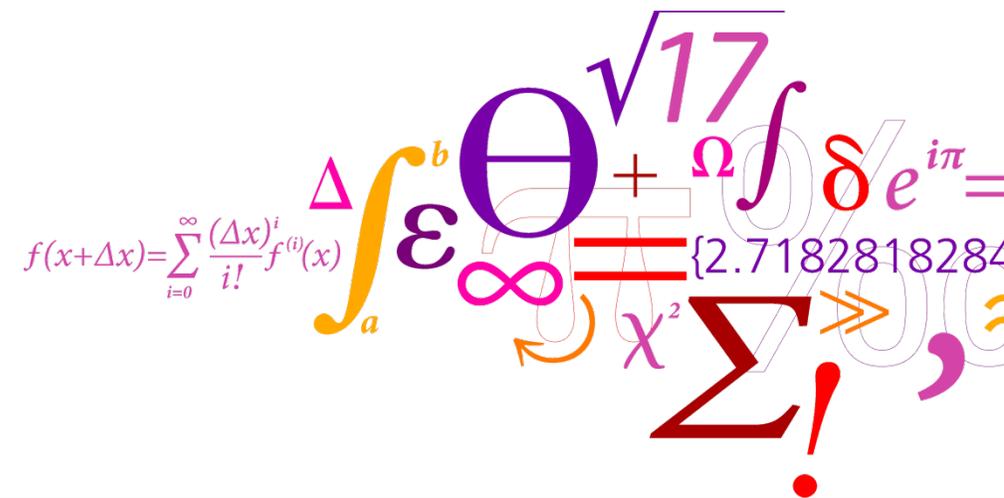


Results from EUPT-CF17

Incurring and spiked pesticides in Wheat Kernels

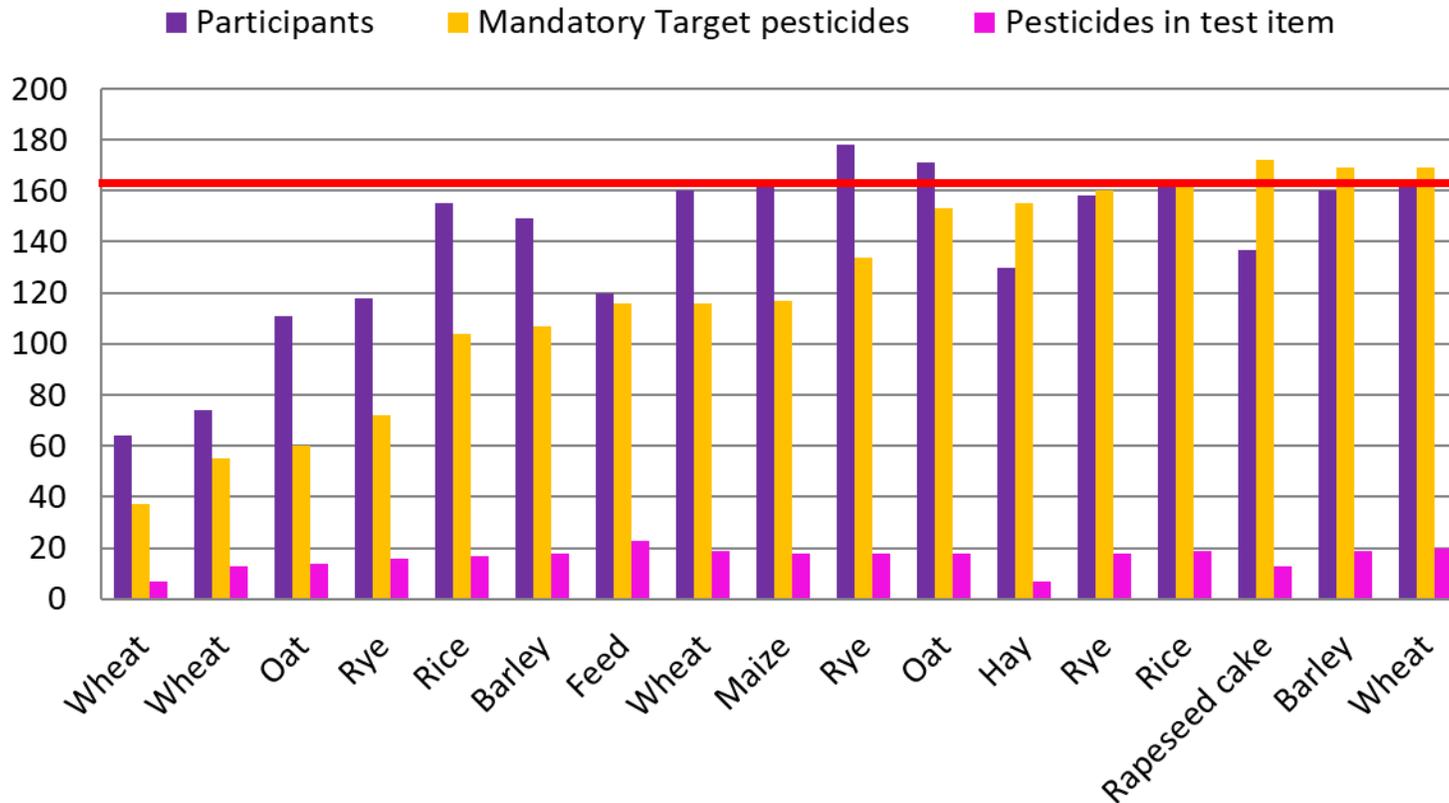
Mette Erecius Poulsen, Elena Hakme and Ederina Ninga

Stuttgart, 18 October 2023



EUPTs on cereals/feeds

Overview of PTs on cereals/feed



	2023 EUPT-CF17
Test material	Wheat
Participants	149(162)
Compulsory target pesticides	169
Voluntary target pesticides	58
Incurred pesticides	16
Spiked pesticides	4
Total no. of pesticides	20

EUPT-CF17 - Announcement

7 November 2022

The European Union Reference Laboratory for Pesticides Residues in Cereals and Feedingstuff (EURL-CF) announces its 17th European Proficiency Test on for pesticides in cereals/feeds requiring multi residue methods (MRMs), EUPT-CF17.

The aim of the test is to provide laboratories with an assessment of their analytical performance and the reliability of their data - in comparison to other laboratories. This will hopefully result in positive changes and quality improvements at each of the laboratories.

Test Items

The Test Material will be **wheat kernels with incurred and spiked pesticides**. The participants will receive approximately 100 g of a treated test material.

Target Analytes

The list of analytes potentially contained in the Test Item is shown in the **Target Pesticides List**. For each of the analytes a specific minimum required reporting level (MRRL) is given.

Registration

The Registration Website is open from late November to 9 January 2023. More information will be published on www.eurl-pesticides.eu

Compound selection/deselection

The webtool will be accessible for selection of compound from 23 January to 6 February 2023.

Shipment and deadline for result submission

The **shipment of Test Items is planned to 6 February 2023** and **deadline for result submission is 6 March 2023**. If any laboratories have holidays during the shipment period, please inform us so that we can rearrange the shipment.

CALENDAR for the EUPT-CF17

Last updated: 03 November 2022

Activity	Dates
Announcement Calendar Target Pesticide List	November 2022
EUPT-Registration Website open	December 2022
Deadline for registration	9 January 2023
Specific Protocol published	23 January 2023
Website for selecting pesticide scope open	23 January 2023
Website for selecting pesticide scope closed	6 February 2023
Distribution of Test items	6 February 2023
Deadline for receipt and acceptance of Test Materials	within 24 hr on receipt
Deadline for Result Submission	6 March 2023 at 23.00 CET
Deadline for submission of additional method information for false negative results	15 March 2023 at 24.00 CET
Preliminary Report (only compilation of results) published	15 May 2023
Final Report published	December 2023

Contact: eurl-cf@food.dtu.dk

Target list – 0 new mandatory pesticides and 6 new voluntary pesticides

- Azadirachtin
- Cyflumetofen
- Diuron
- Forchlorfenuron
- Metaldehyde
- Phenmedipham



EUPT-CF17 Pesticide Target List

(last updated: 02.11.2022)

New compounds on the list is marked with red

Pesticide no.	Pesticides	MRRL	Additional information: Residue definitions or isomers to analyse	Webtool name
Compulsory Compounds (will be considered in Category A/B classification)				
1	2-phenylphenol	0.01	Orthophenylphenol (Free compound only)	Orthophenylphenol
2	Acephate	0.01		Acephate
3	Aclonifen	0.01		Aclonifen
4	Acetamiprid	0.01		Acetamiprid
5	Acrinathrin	0.01		Acrinathrin
6	Aldrin	0.005		Aldrin
7	Ametoctradin	0.01		Ametoctradin
8	Azinphos-methyl	0.005		Azinphos-methyl
9	Azoxystrobin	0.01		Azoxystrobin
10	Bifenthrin	0.01		Bifenthrin
11	Biphenyl	0.01		Biphenyl
12	Bitertanol	0.01	Bitertanol (sum of isomers)	Bitertanol
13	Bixafen	0.01		Bixafen
14	Boscalid	0.01		Boscalid

	Country	Number of labs
EU	Austria	1
	Belgium	3
	Bulgaria	1
	Croatia	8
	Cyprus	2
	Czech Republic	3
	Denmark	1
	Estonia	1
	Finland	2
	France	8
	Germany	26
	Greece	3
	Hungary	4
	Ireland	1
	Italy	21
	Latvia	1
	Lithuania	1
	Luxembourg	1
	Netherlands	4
Poland	13	
Portugal	2	
Romania	4	

	Country	Number of labs
EU	Slovakia	3
	Slovenia	2
	Spain	26
	Sweden	2
	EU	144

EFTA		
	Iceland	1
	Norway	2
	Switzerland	2
		5
	EU + EFTA	149

3Countries		
	Argentina	1
	Australia	1
	Egypt	1
	India	1
	Peru	2
	Thailand	1
	United Kingdom	1
Candidate	Serbia	5
Potential candidate		
	Non EU	13

Grand total	162
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7 labs didn't report results. 6 of them where from EU.

34 out of 35 NRLs participated, Denmark (EURL), Malta (?) Bulgaria (No NRL-CF)

Test material

- Wheat kernels
- Grown in Denmark in 2022

11 Fungicides

7 Insecticides

2 Herbicides

Pesticide		Field application	Spike in laboratory	Formulation or standard
Azoxystrobin		x		Amistar/Amistar gold
Bixafen		x		Ascra Xpro
Clomazone	Voluntary	x		Clomate
Cyazofamid		x	x	Ranman Top/Analytical standard
Cyfluthrin			x	Analytical standard
Cyprodinil		x		Kayak
Difenoconazole		x		Amistar gold
Dimethomorph		x		Cabrio Duo
Flonicamid		x		Teppeki
Fluapyram		x		Ascra Xpro
HCH-beta	Voluntary		x	Analytical standard
Metconazole		x		Juventus
Phenmedipham	Voluntary		x	Analytical standard
Pirimicarb		x		Pirimor
Pirimicarb-desmethyl			x	Analytical standard
Proquinazid		x		Talius
Prothioconazole		x		Ascra Xpro/Kayak/Madison
Pyraclostrobin		x		Cabrio Duo
Pyriproxyfen		x	x	Admiral/Analytical standard
Trifloxystrobin		x		Madison

20

16

Spike procedure and mixing



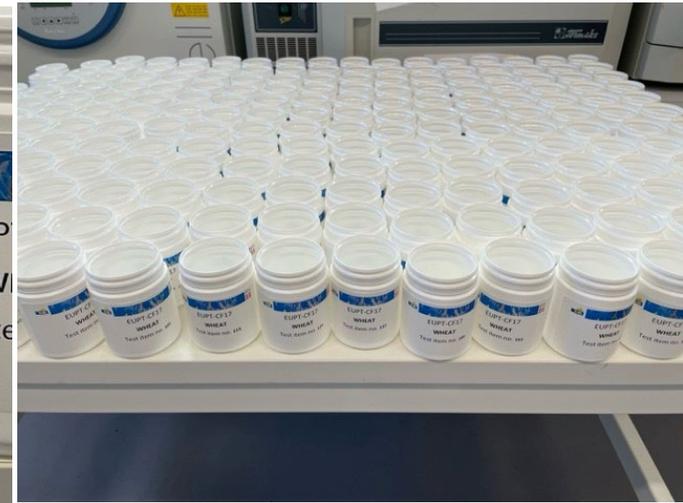
7 x 1.4 kg

- Cyazofamid (overspike)
- Cyfluthrin
- HCH-beta
- Phenmedipham
- Pirimicarb-desmethyl
- Pyriproxyfen (overspike)



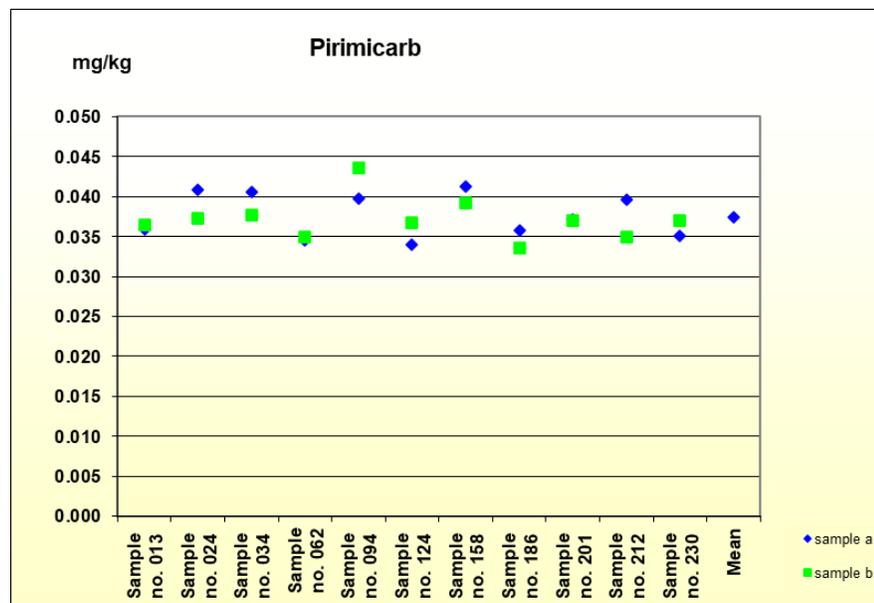
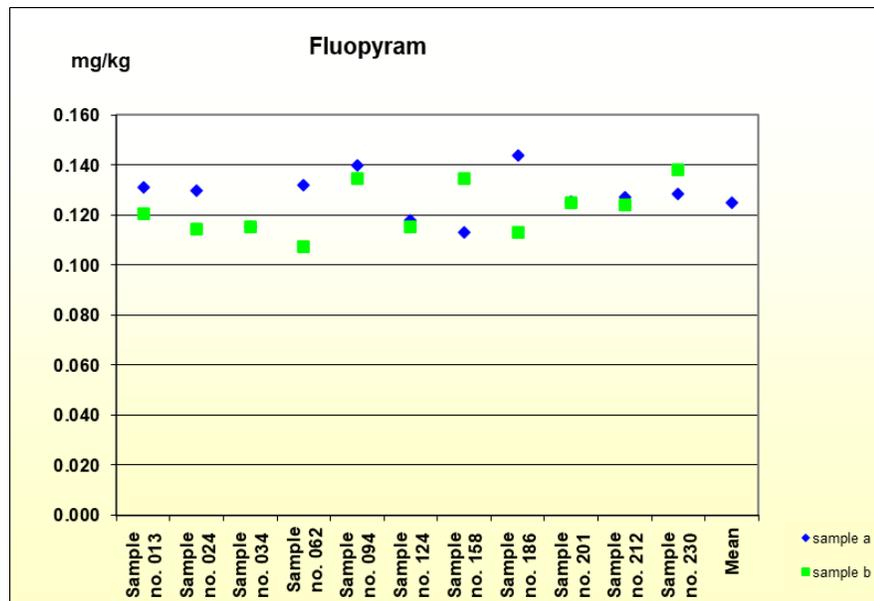
Packing and sample shipment

- Amount of sample: 100 gram
- Shipment date: 6 February 2023



Homogeneity test

	Mean, mg/kg	S_s^2	c	$S_s^2 < c$
Azoxystrobin	0.210	0.00021	0.0007	Pass
Bixafen	0.085	0.00000	0.0002	Pass
Clomazone	0.032	0.00000	0.0000	Pass
Cyazofamid	0.221	0.00009	0.0008	Pass
Cyflutrin	0.069	0.00002	0.0001	Pass
Cyprodinil	0.342	0.00000	0.0027	Pass
Difenoconazole	0.094	0.00000	0.0002	Pass
Dimethomorph	0.165	0.00000	0.0005	Pass
Fonicamid	0.043	0.00000	0.0000	Pass
Fluopyram	0.125	0.00000	0.0003	Pass
HCH-beta	0.042	0.00001	0.0001	Pass
Metconazole	0.060	0.00000	0.0001	Pass
Phenmedipham	0.071	0.00002	0.0001	Pass
Pirimicarb	0.037	0.00000	0.0000	Pass
Pirimicarb-desmethyl	0.056	0.00001	0.0000	Pass
Prothioconazole-desthio	0.192	0.00014	0.0006	Pass
Pyraclostrobin	0.109	0.00002	0.0002	Pass
Pyriproxyfen	0.049	0.00001	0.0001	Pass
Trifloxystrobin	0.050	0.00000	0.0000	Pass

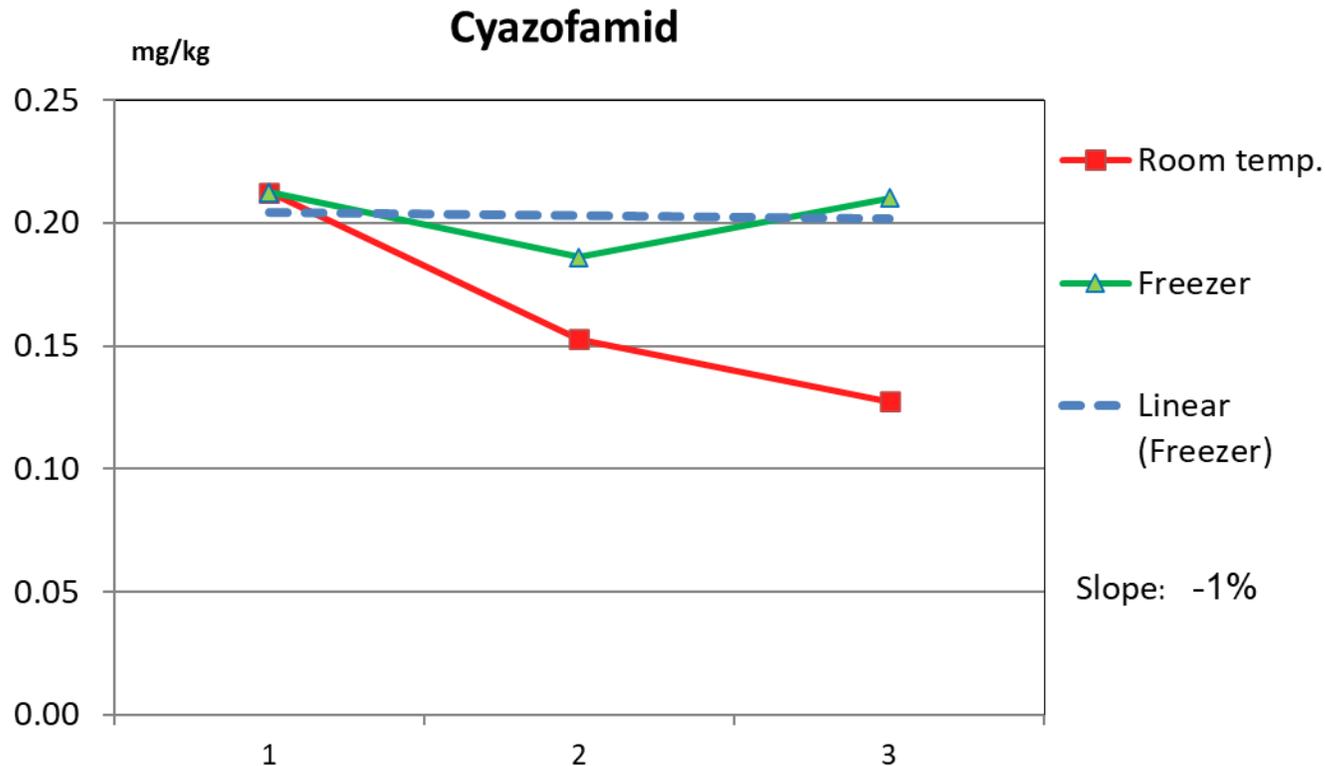




Stability

	Mean, mg/kg	Storage at -18 degrees			Storage at room temperature		
		$ x_1 - y_i $	$0.3 \times \sigma$	$ x_1 - y_i \leq 0.3 \times \sigma$	$ x_1 - y_i $	$0.3 \times \sigma$	$ x_1 - y_i \leq 0.3 \times \sigma$
Azoxystrobin	0.234	0.008	0.018	Pass	0.006	0.018	Pass
Bixafen	0.096	0.003	0.008	Pass	0.000	0.008	Pass
Clomazone	0.045	0.000	0.003	Pass	0.001	0.003	Pass
Cyazofamid	0.203	0.002	0.003	Pass	0.085	0.003	NO
Cyflutrin	0.115	0.007	0.005	Pass	0.013	0.005	Pass
Cyprodinil	0.549	0.004	0.028	Pass	0.003	0.028	Pass
Difenoconazole	0.099	0.003	0.008	Pass	0.007	0.008	Pass
Dimethomorph	0.207	0.014	0.014	Pass	0.004	0.014	Pass
Fonicamid	0.100	0.003	0.004	Pass	0.005	0.004	Pass
Fluopyram	0.146	0.004	0.012	Pass	0.001	0.012	Pass
HCH-beta	0.051	0.001	0.004	Pass	0.000	0.004	Pass
Metconazole	0.076	0.000	0.006	Pass	0.001	0.006	Pass
Phenmedipham	0.061	0.001	0.005	Pass	0.002	0.005	Pass
Pirimicarb	0.036	0.003	0.003	Pass	0.000	0.003	Pass
Pirimicarb-desmethyl	0.051	0.001	0.005	Pass	0.002	0.005	Pass
Proquinazid	0.080	0.003	0.007	Pass	0.005	0.007	Pass
Prothioconazole-desthio	0.187	0.006	0.014	Pass	0.003	0.014	Pass
Pyraclostrobin	0.106	0.004	0.085	Pass	0.005	0.085	Pass
Pyriproxyfen	0.063	0.003	0.005	Pass	0.001	0.005	Pass
Trifloxystrobin	0.048	0.002	0.004	Pass	0.000	0.004	Pass

Not stable at room temperature

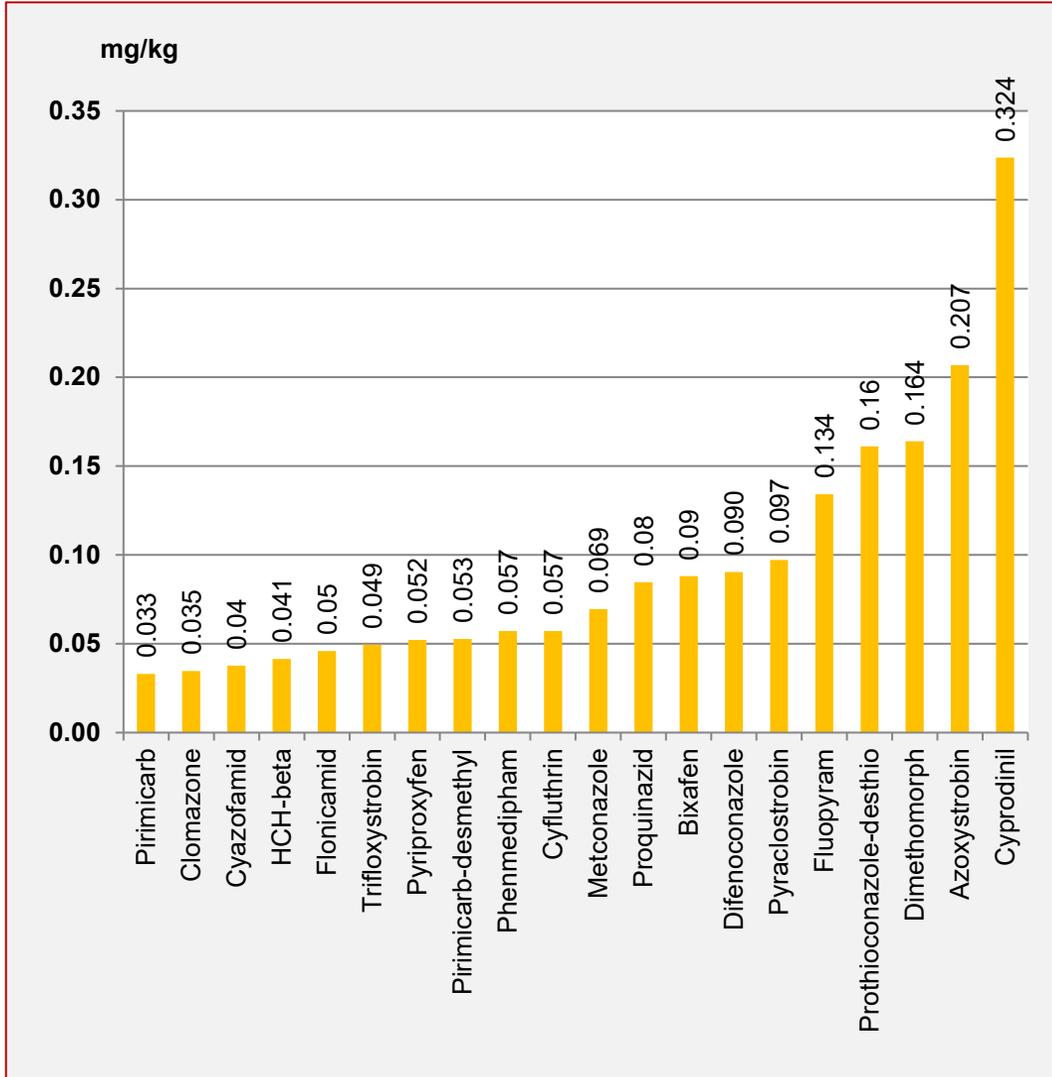


- Aqueous Photolytic Stability (DT50):
- Cyazofamid: 0.5 h
- Azoxystrobin: 8.7–13.9 d (pH 7)
- Chlorpyrifos: 29.6 d (25 °C)

Assigned values

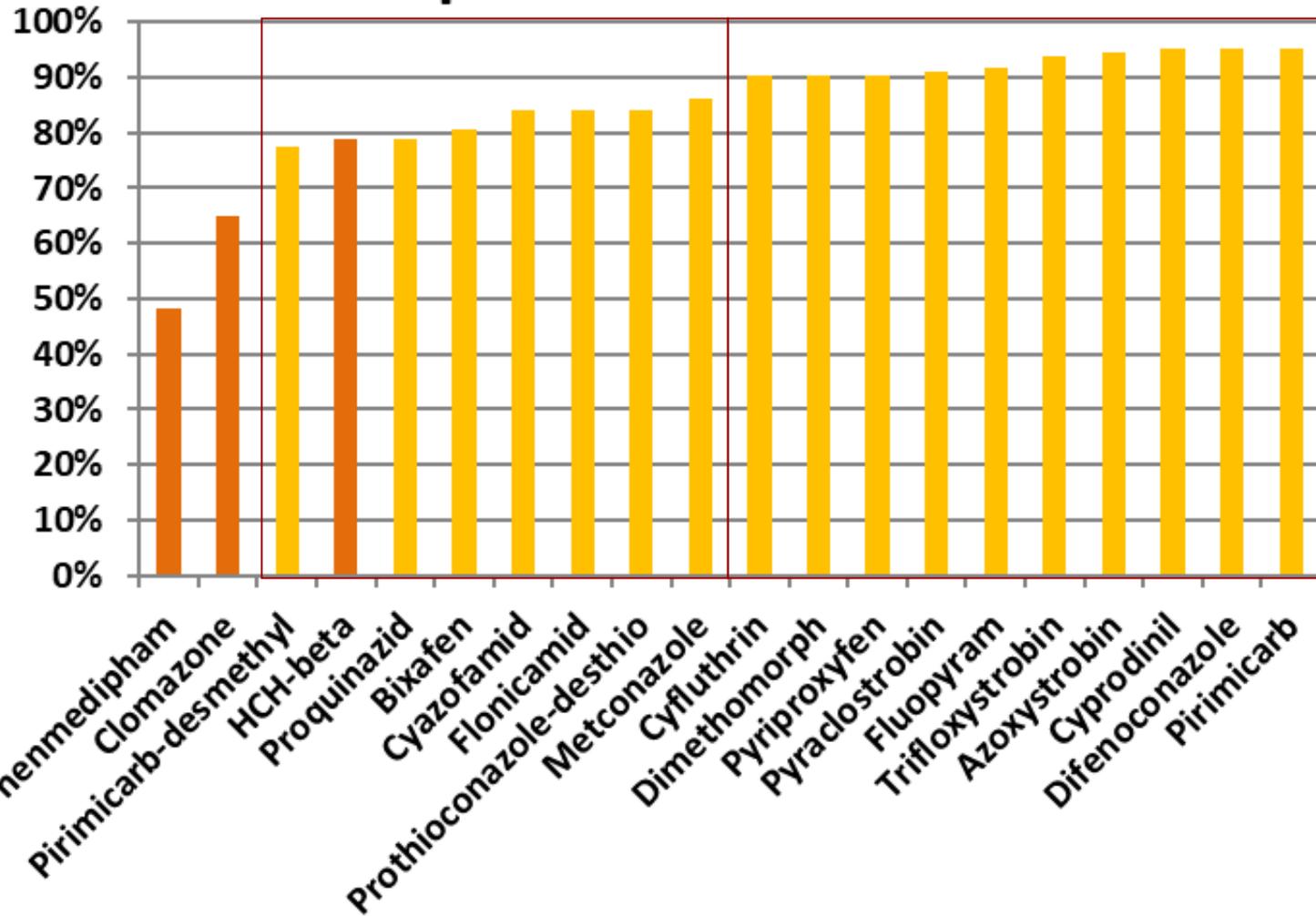
- Algorithm A mean of results from EU and EFTA laboratories
- Outliers
 - Only obvious incorrect results (10x)
 - Azoxystrobin: 4.714 (23x)
 - Cyazofamid: 0.455 (12x)
 - Pirimicarb: 0.675 (21x)
- Uncertainty
 - $u=1.25 \cdot (s^* / \sqrt{n})$
 - s^* is robust standard deviation (Alg A standard deviation)
 - N is the number of participants

PESTICIDES	Assigned values mg/kg
Azoxystrobin	0.207
Bixafen	0.088
Clomazone	0.035
Cyazofamid	0.038
Cyfluthrin	0.057
Cyprodinil	0.324
Difenoconazole	0.090
Dimethomorph	0.164
Flonicamid	0.046
Fluopyram	0.134
HCH-beta	0.041
Metconazole	0.069
Phenmedipham	0.057
Pirimicarb	0.033
Pirimicarb-desmethyl	0.053
Proquinazid	0.085
Prothioconazole-desthio	0.161
Pyraclostrobin	0.097
Pyriproxyfen	0.052
Trifloxystrobin	0.049



PESTICIDES	Assigned values mg/kg
Azoxystrobin	0.207
Bixafen	0.088
Clomazone	0.035
Cyazofamid	0.038
Cyfluthrin	0.057
Cyprodinil	0.324
Difenoconazole	0.090
Dimethomorph	0.164
Flonicamid	0.046
Fluopyram	0.134
HCH-beta	0.041
Metconazole	0.069
Phenmedipham	0.057
Pirimicarb	0.033
Pirimicarb-desmethyl	0.053
Proquinazid	0.085
Prothioconazole-desthio	0.161
Pyraclostrobin	0.097
Pyriproxyfen	0.052
Trifloxystrobin	0.049

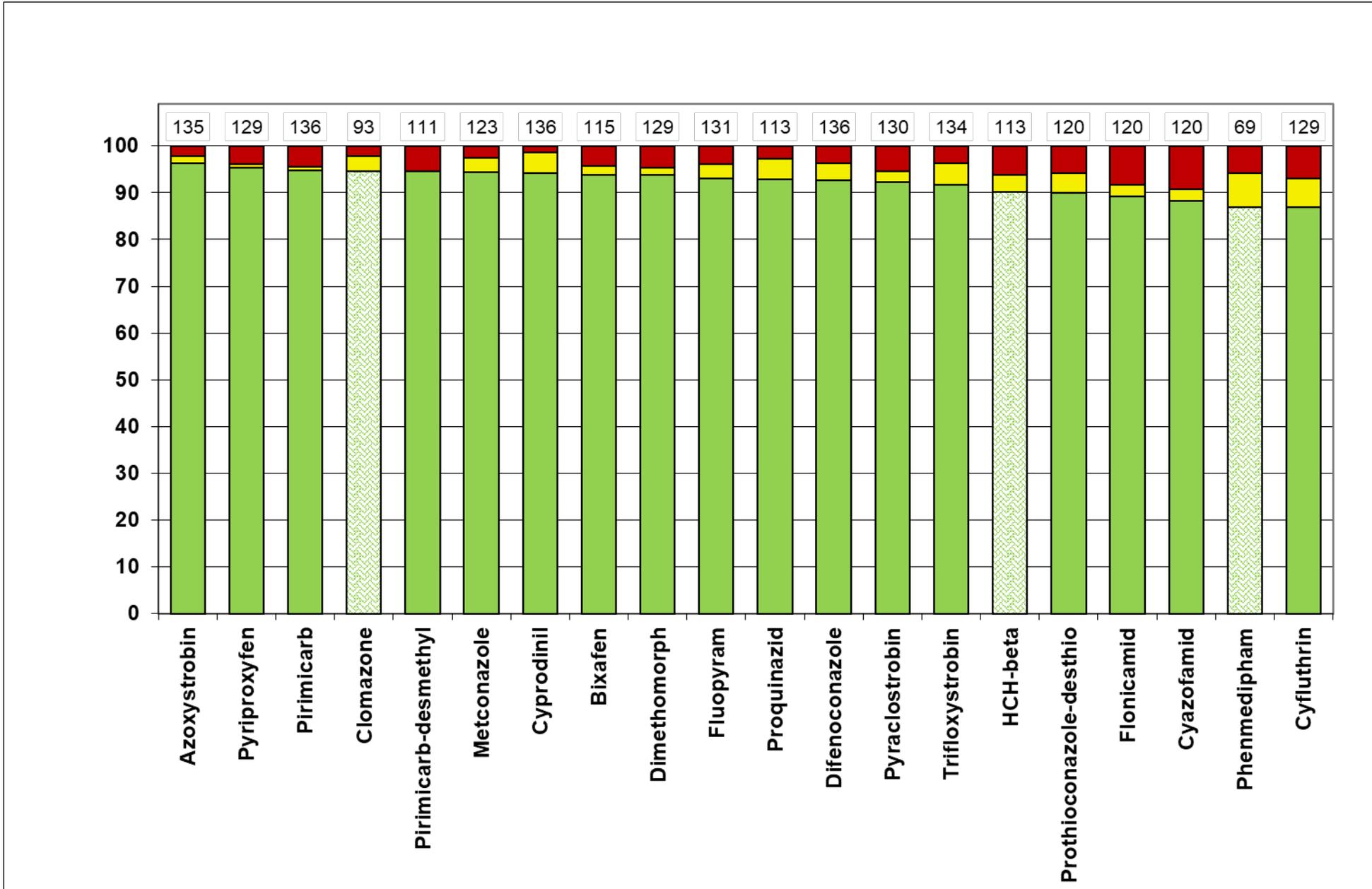
Reported results %





	No. of reported results	Assigned values	Acceptable %	Questionable %	Unacceptable %	False negatives %
Azoxystrobin	135	0.207	96	1	2	1
Bixafen	115	0.088	94	2	4	3
Clomazone	93	0.035	95	3	2	1
Cyazofamid	120	0.038	88	3	9	5
Cyfluthrin	129	0.057	87	6	7	5
Cyprodinil	136	0.324	94	4	1	1
Difenoconazole	136	0.090	93	4	4	1
Dimethomorph	129	0.164	94	2	5	1
Flonicamid	120	0.046	89	3	8	5
Fluopyram	131	0.134	93	3	4	1
HCH-beta	113	0.041	90	4	6	3
Metconazole	123	0.069	94	3	2	1
Phenmedipham	69	0.057	87	7	6	0
Pirimicarb	136	0.033	95	1	4	1
Pirimicarb-desmethyl	111	0.053	95	0	5	5
Proquinazid	113	0.085	93	4	3	0
Prothioconazole-desthio	120	0.161	90	4	6	4
Pyraclostrobin	130	0.097	92	2	5	4
Pyriproxyfen	129	0.052	95	1	4	2
Trifloxystrobin	134	0.049	92	4	4	1

Average 92 %





	Lab code	Azoxystrobin	Bixafen	Clomazone *)	Cyazofamid	Cyfluthrin	Cyprodinil	Difenoconazole	Dimethomorph	Flonicamid	Fluopyram	HCH-beta *)	Metconazole	Pirimicarb	Pirimicarb-desmethyl	Prothioconazole-desthio	Pyraclostrobin	Pyriproxyfen	Trifloxystrobin	
1	10					1														1
2	11				1							1								2
3	13		1																	1
4	30															1				1
5	38				1			1		1										3
6	41					1														1
7	43									1										1
8	48					1										1				2
9	50													1						1
10	53			1																1
11	58									1										1
12	61															1				1
13	64	1		1		1		1					1			1		1	1	8
14	65																1			1
15	82														1					1
16	86				1															1
17	94											1								1
18	101																		1	1
19	103	1			1		1	1	1				1	1			1	1	1	10
20	104											1								1
21	107				1															1
22	109				1					1					1		1			4
23	116					1														1
24	120					1														1
25	129									1										1
26	135		1												1					2
27	150															1				1
28	154																1			1
29	170		1			1				1	1				1	1	1	1		8
	29	2	3	2	6	7	1	3	1	6	1	3	2	1	5	6	5	3	3	60

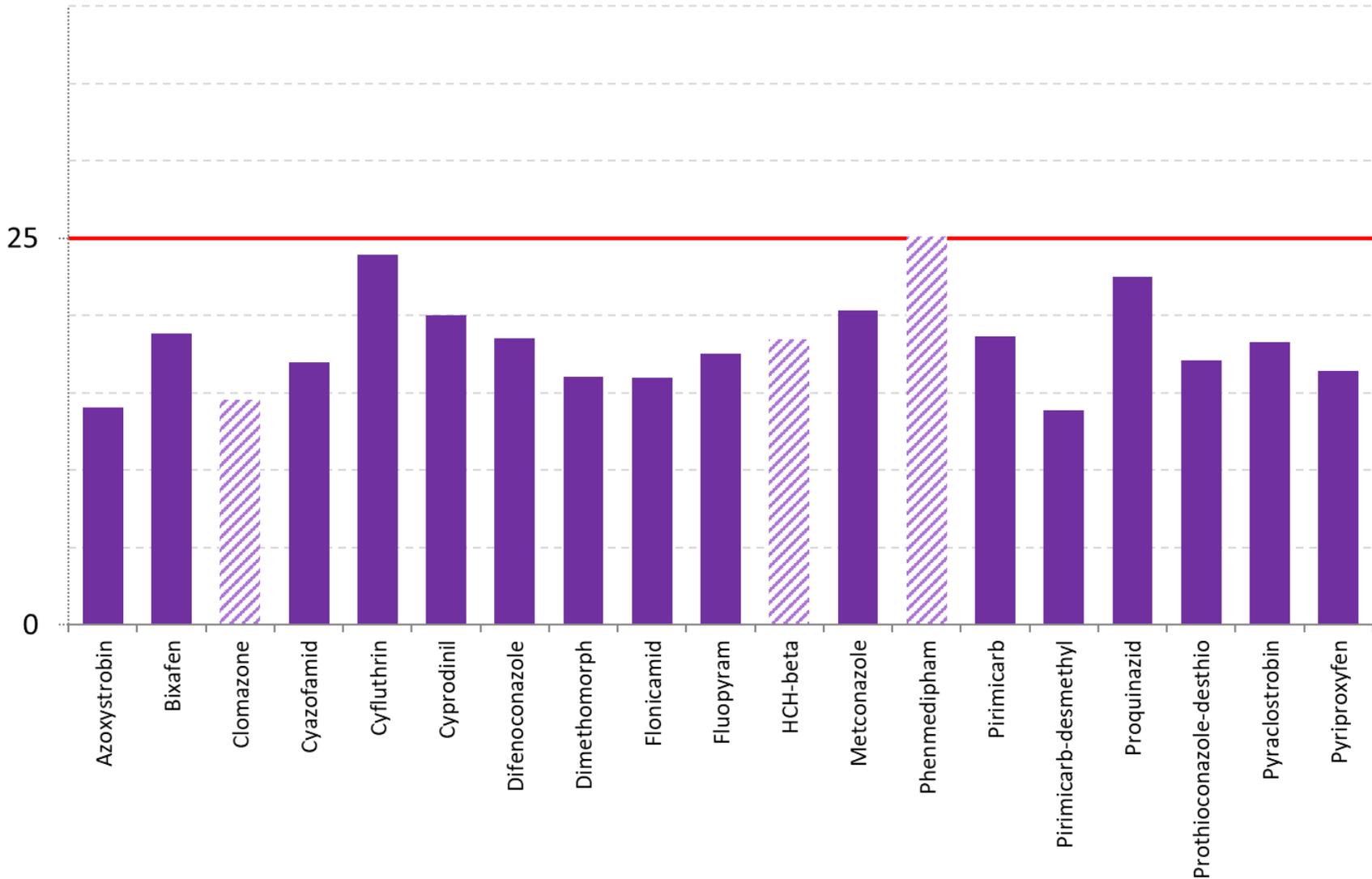
No false negatives:
Phenmedipham
Proquinazid

False positives

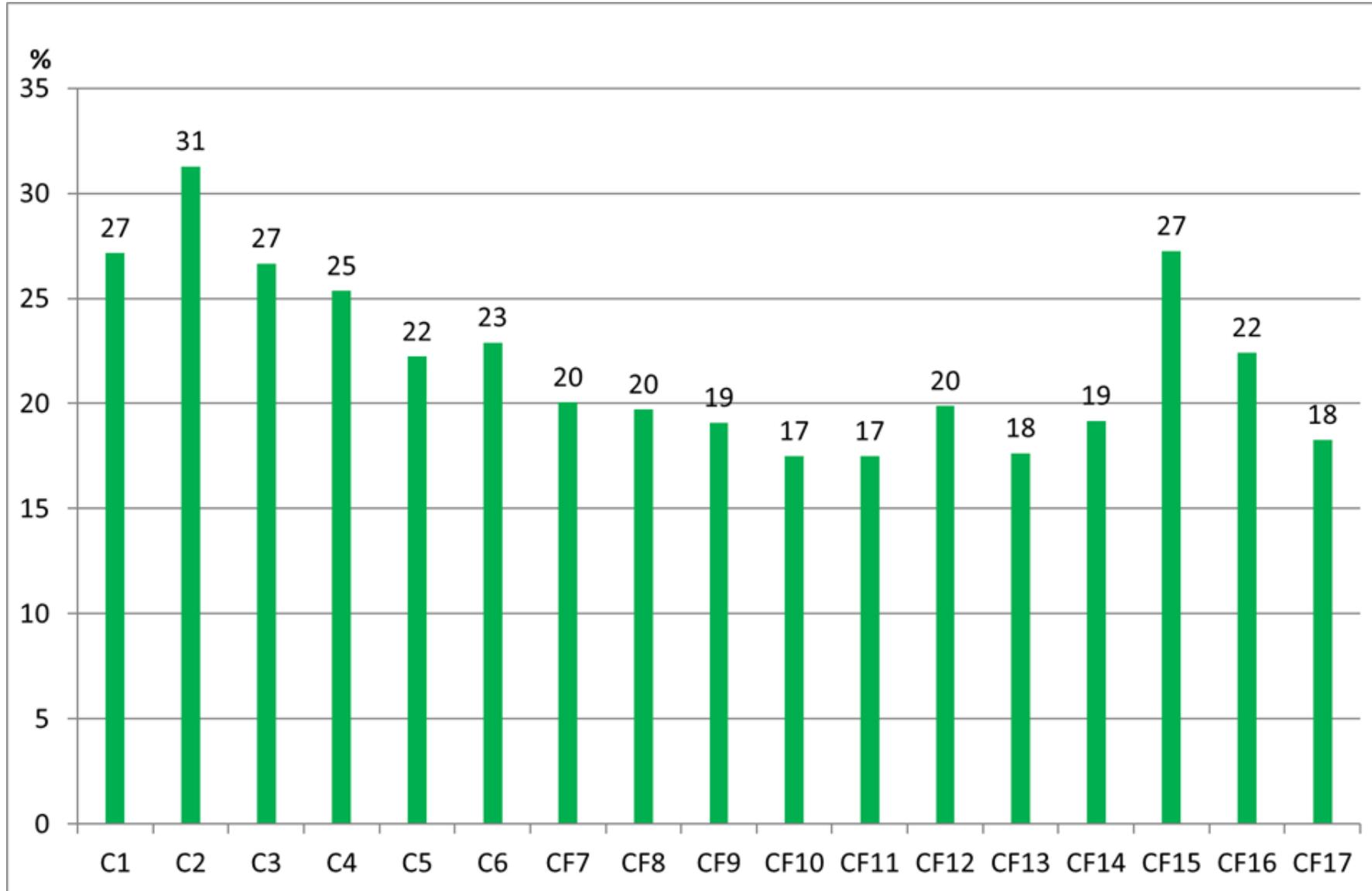
Lab code	Pesticide	Concentration mg/kg	Determination technique	RL, mg/kg
38	Acephate	2.447	LC-MS/MS QQQ	0.01
43	Acetamiprid	0.006	LC - MS/MS	0.004
41	Biphenyl	0.024	GC-MS/MS (QQQ)	0.01
11	Lindane	0.037	GC-MS/MS (QQQ)	0.01
24	Lindane	0.011	GC- (μ) ECD	0.01
108	Lindane	0.053	GC-MS/MS (QQQ)	0.01
109	Triadimenol	0.011	GC-MS/MS (QQQ)	0.01



Alg A RSD %



Average	18%
Min	14%
Max	25%



Calculations of z scores

- For each laboratory/pesticide combination :
- $z = (x - X) / \sigma$
- x is the result reported by the participant or the specific reporting limit of the lab for those labs not having detected the pesticide present in the test material
- X is the assigned value, Alg A mean without outliers
- σ is the target standard deviation obtained by multiplying the median by the FFP RSD of 25%
- $|z| \leq 2$ Acceptable
- $2 < |z| < 3$ Questionable
- $|z| \geq 3$ Unacceptable

Category A laboratories

- To be classified as Category A laboratory the labs had to 1) be able to analyse for at least 90% of the compulsory pesticides on the target pesticides list, 2) have correctly detected and quantified at least 90% of the pesticide present in the test material (7 \geq pesticide residues) and 3) report no false positive.
- Evaluation of the overall performance, the Average of the Squared z-Score (AZ^2) are calculated:

$$AZ^2 = \frac{\sum_{i=1}^n Z_i^2}{n}$$

- $z \leq 2$ Good
- $2 < z < 3$ Satisfactory
- $z \geq 3$ Unsatisfactory

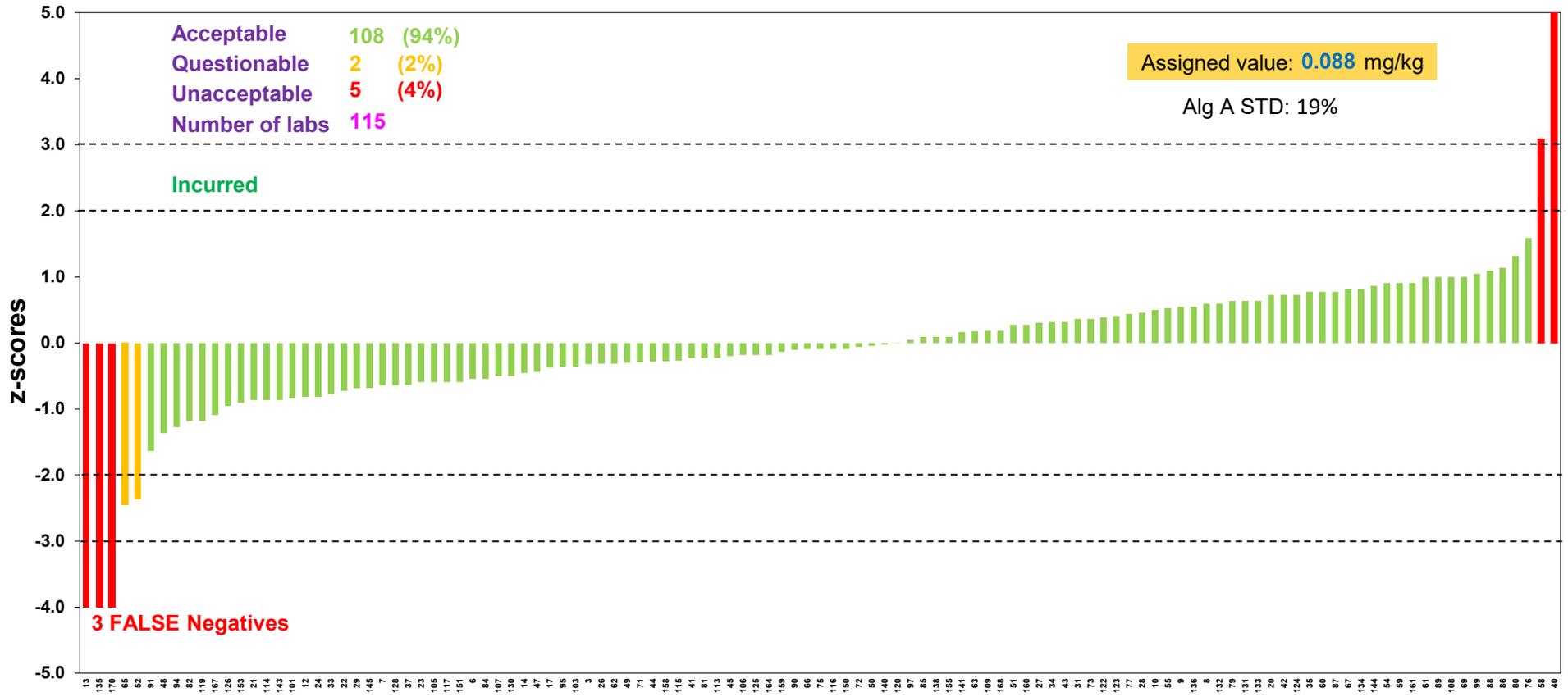
Azoxystrobin

EU and EFTA Laboratories



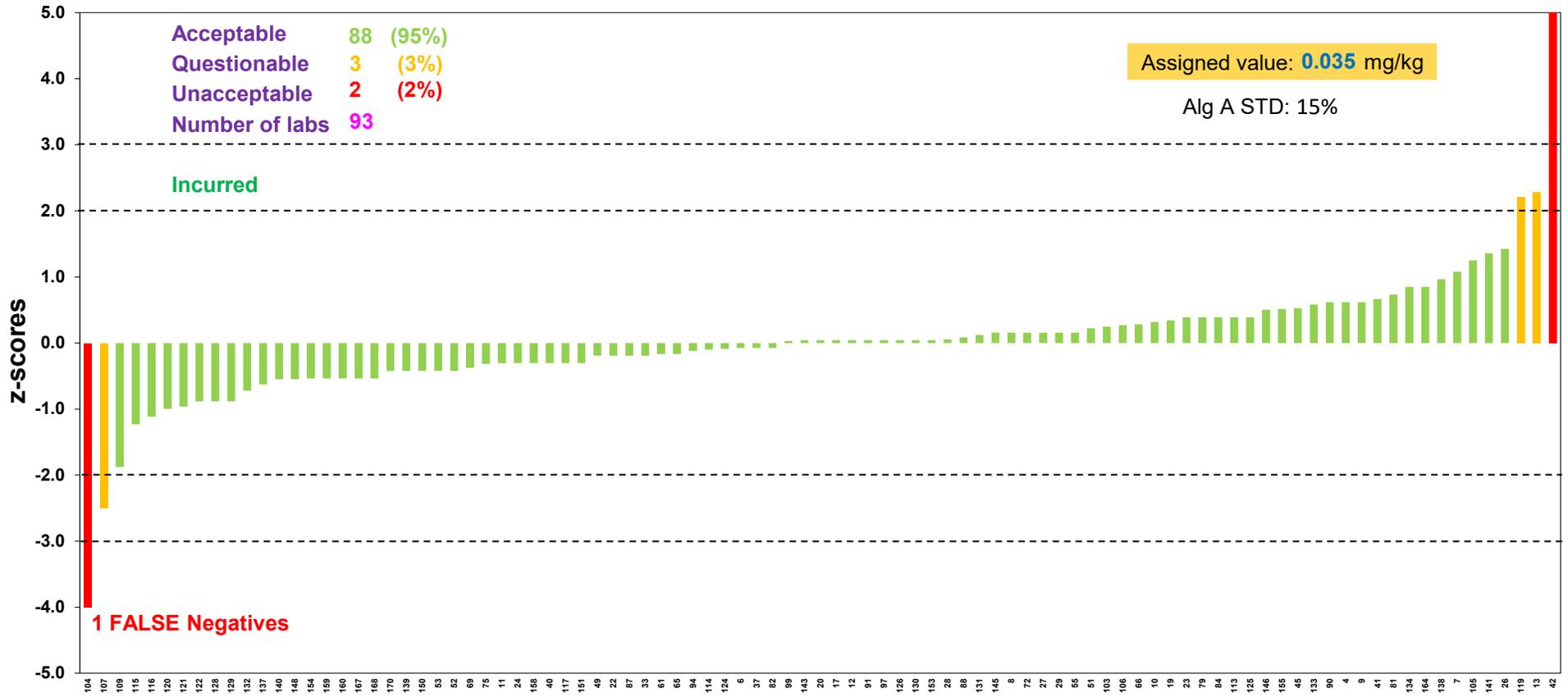
Bixafen

EU and EFTA Laboratories



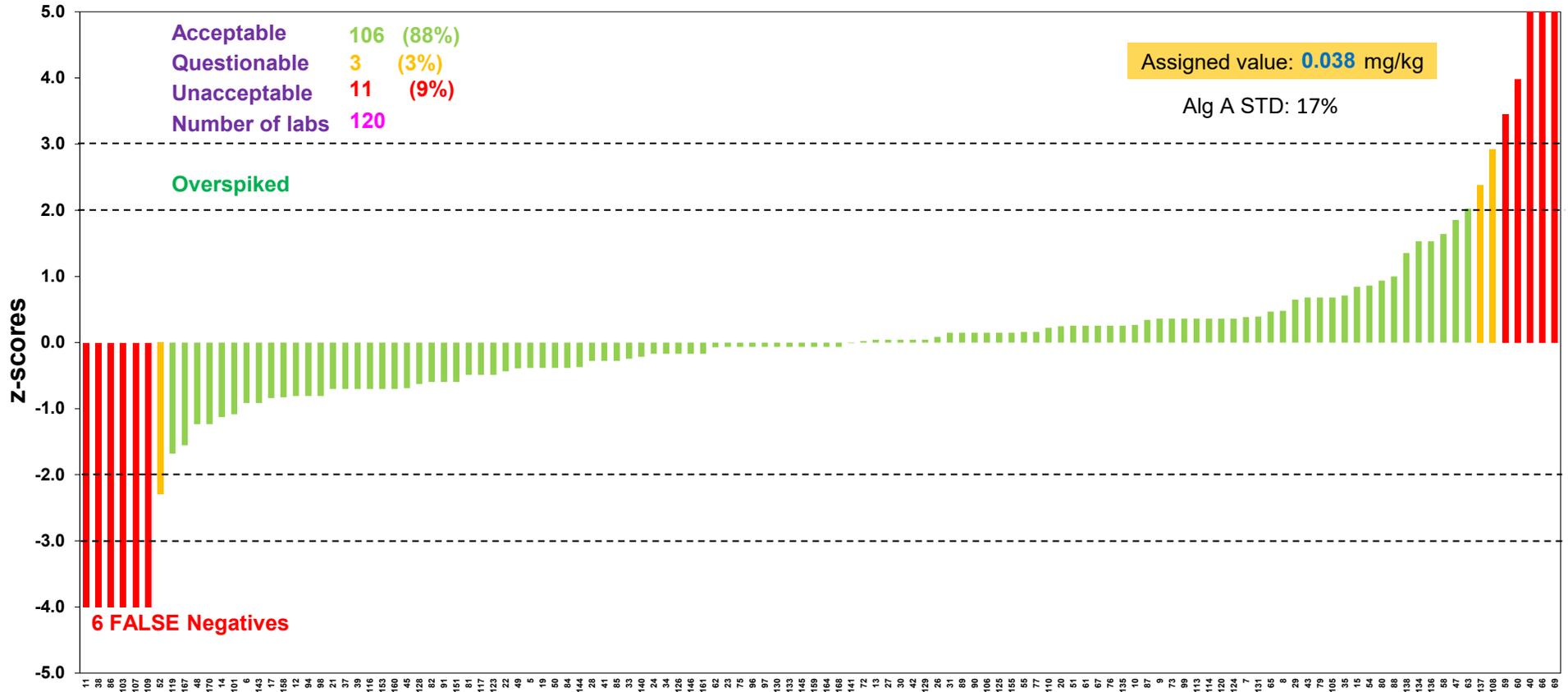
Clomazone

EU and EFTA Laboratories



Cyazofamid

EU and EFTA Laboratories



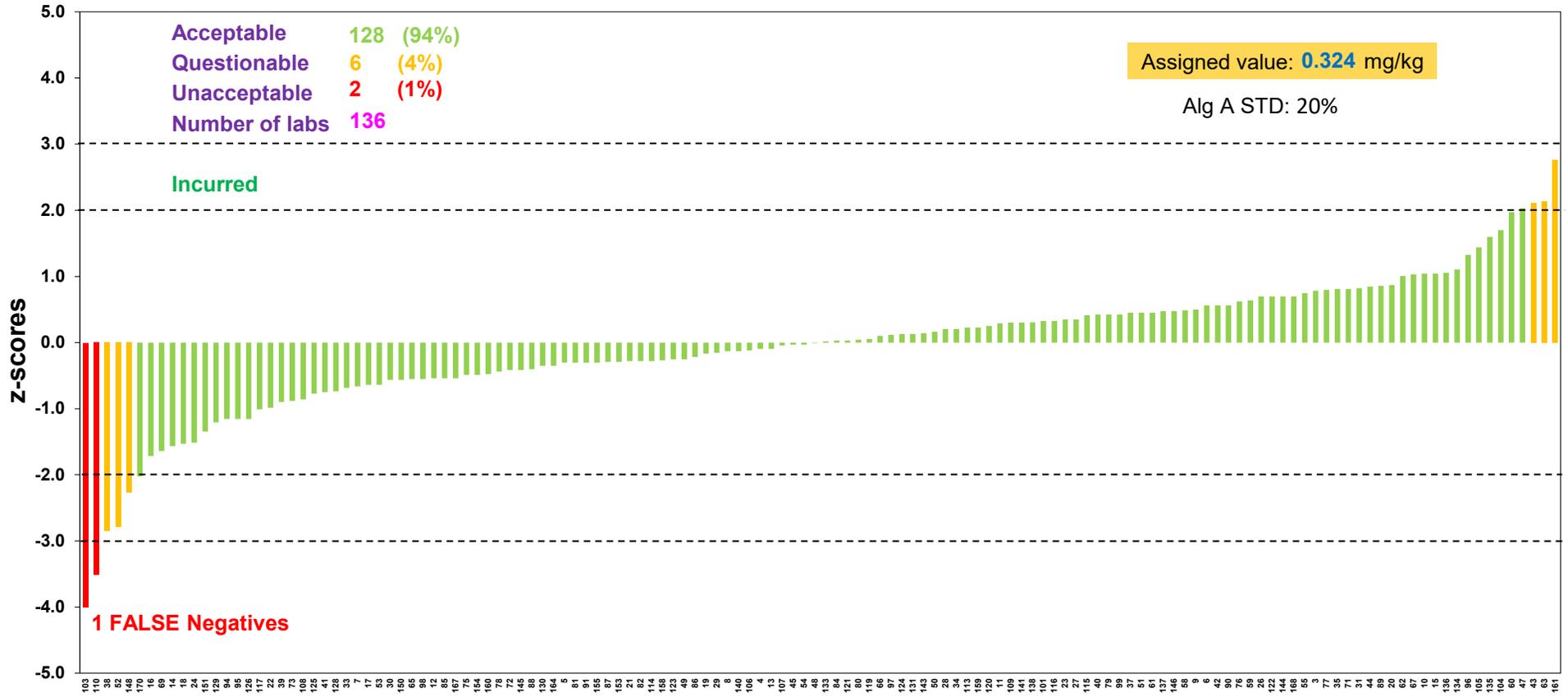
Cyfluthrin

EU and EFTA Laboratories



Cyprodinil

EU and EFTA Laboratories



Difenoconazole

EU and EFTA Laboratories



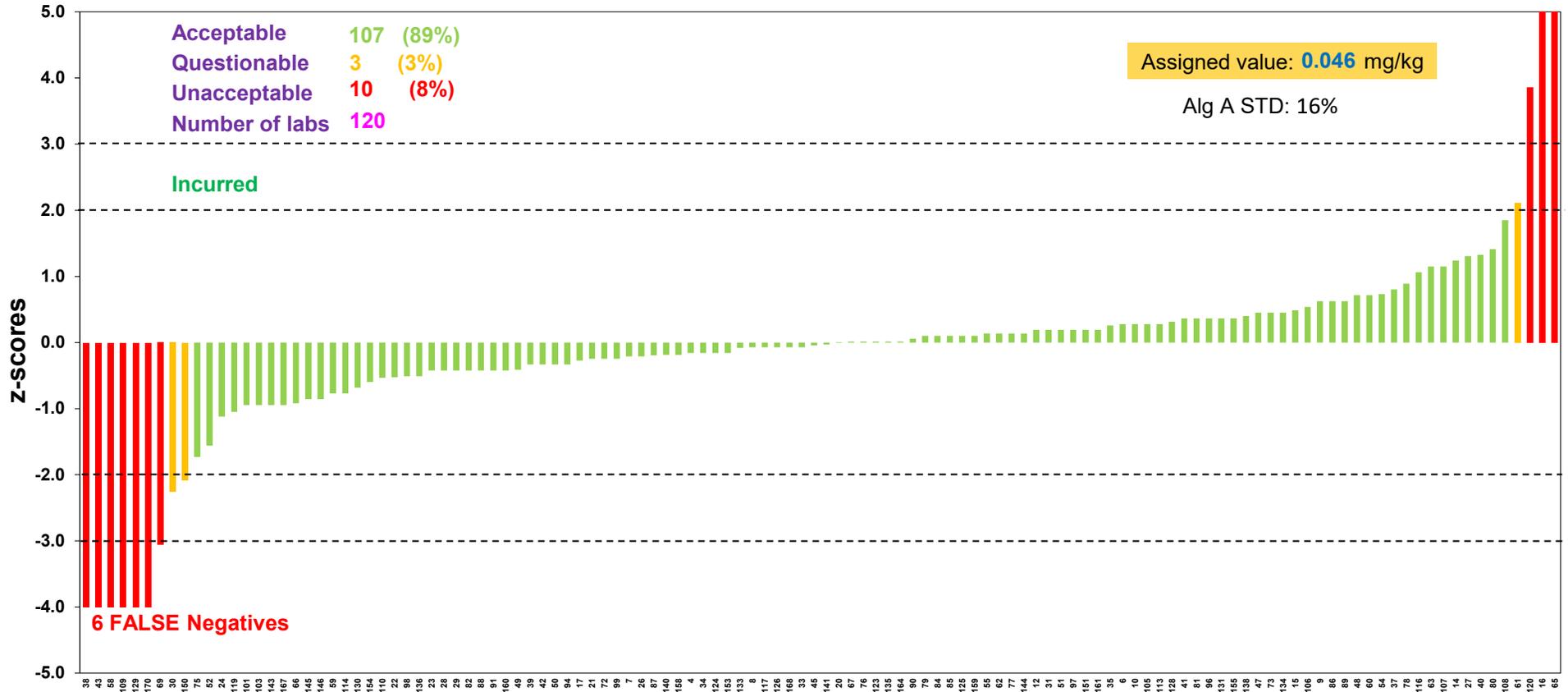
Dimethomorph

EU and EFTA Laboratories



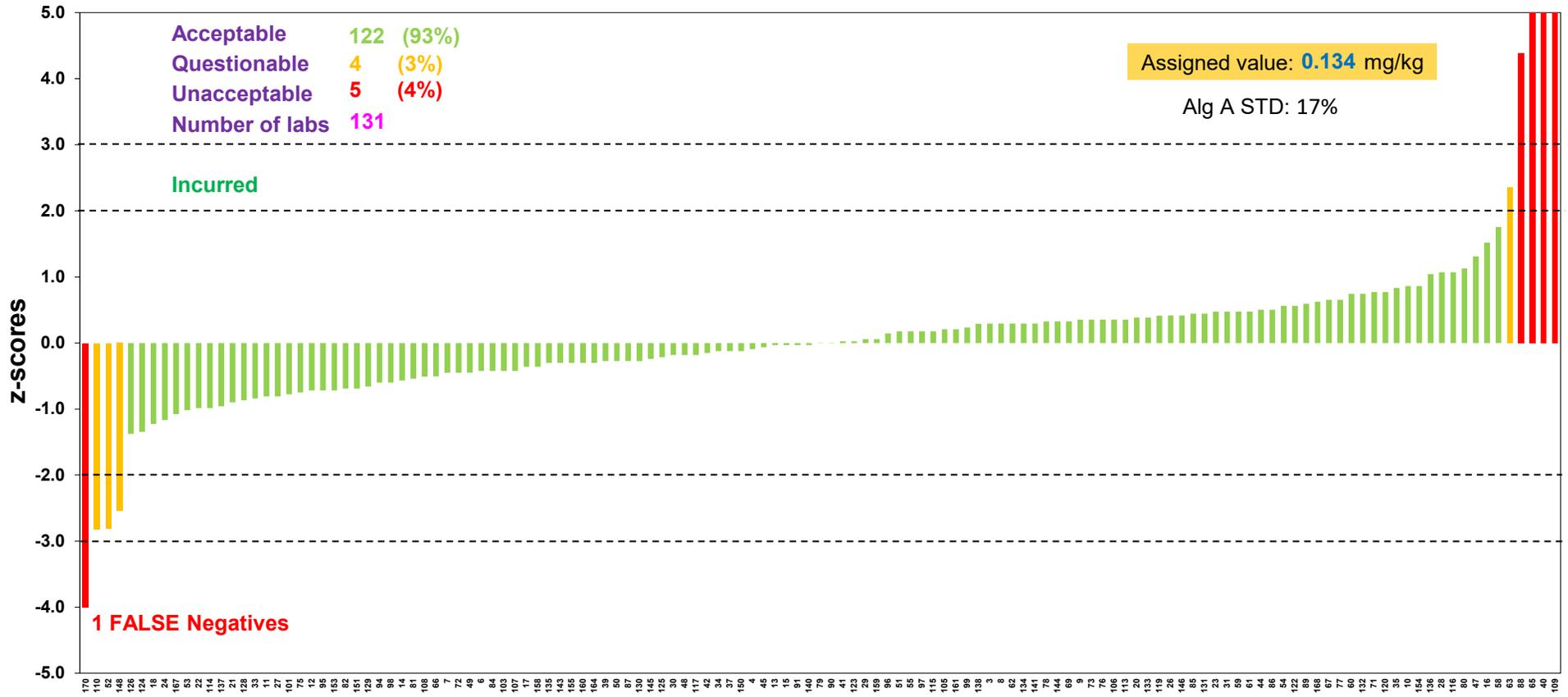
Flonicamid

EU and EFTA Laboratories



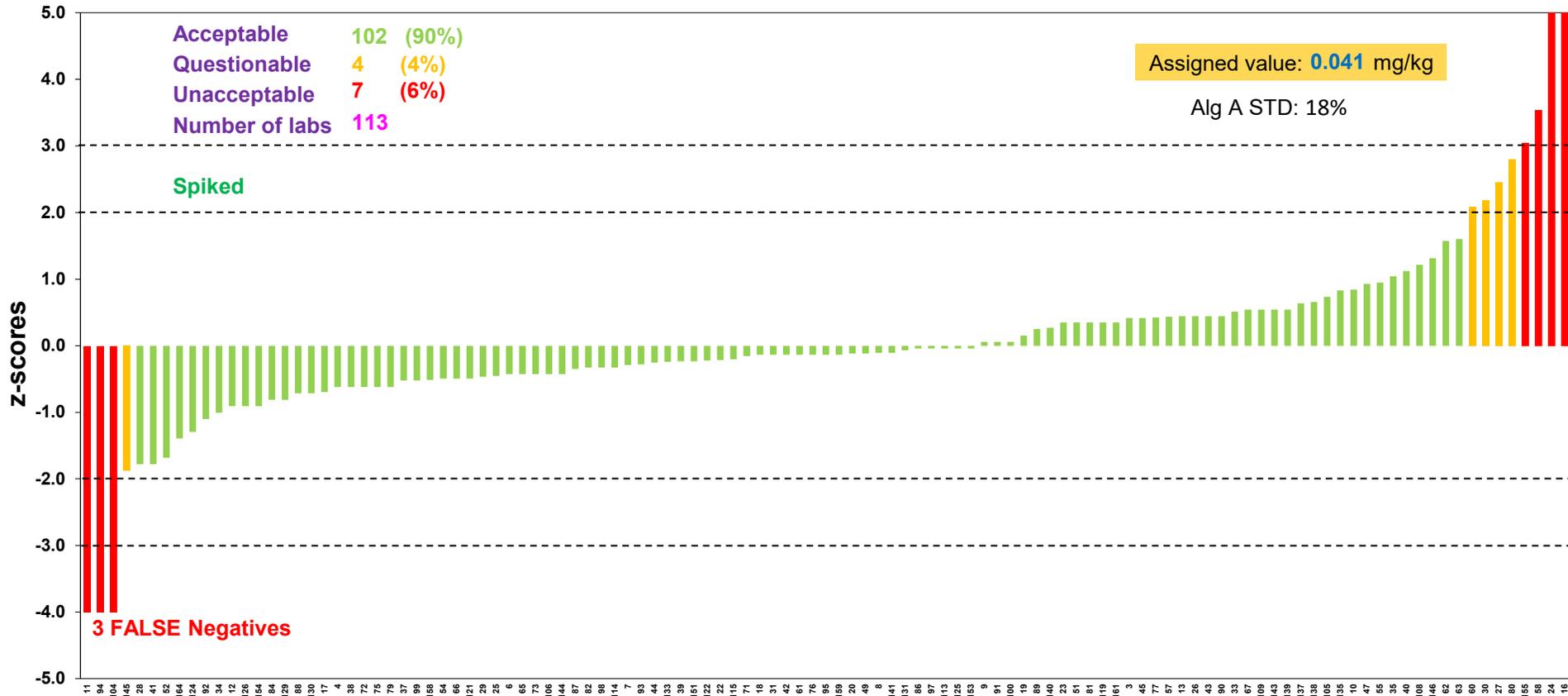
Fluopyram

EU and EFTA Laboratories



HCH-beta

EU and EFTA Laboratories



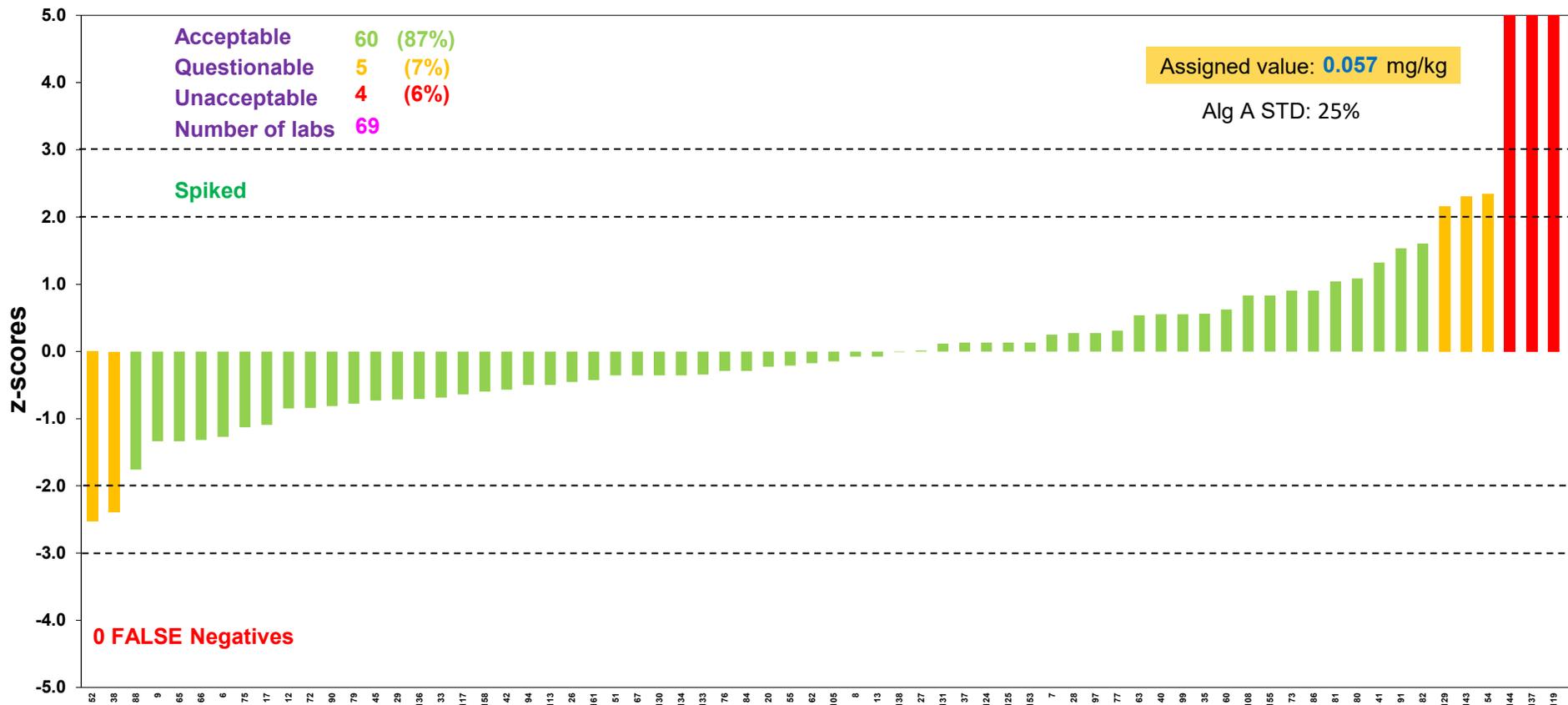
Metconazole

EU and EFTA Laboratories



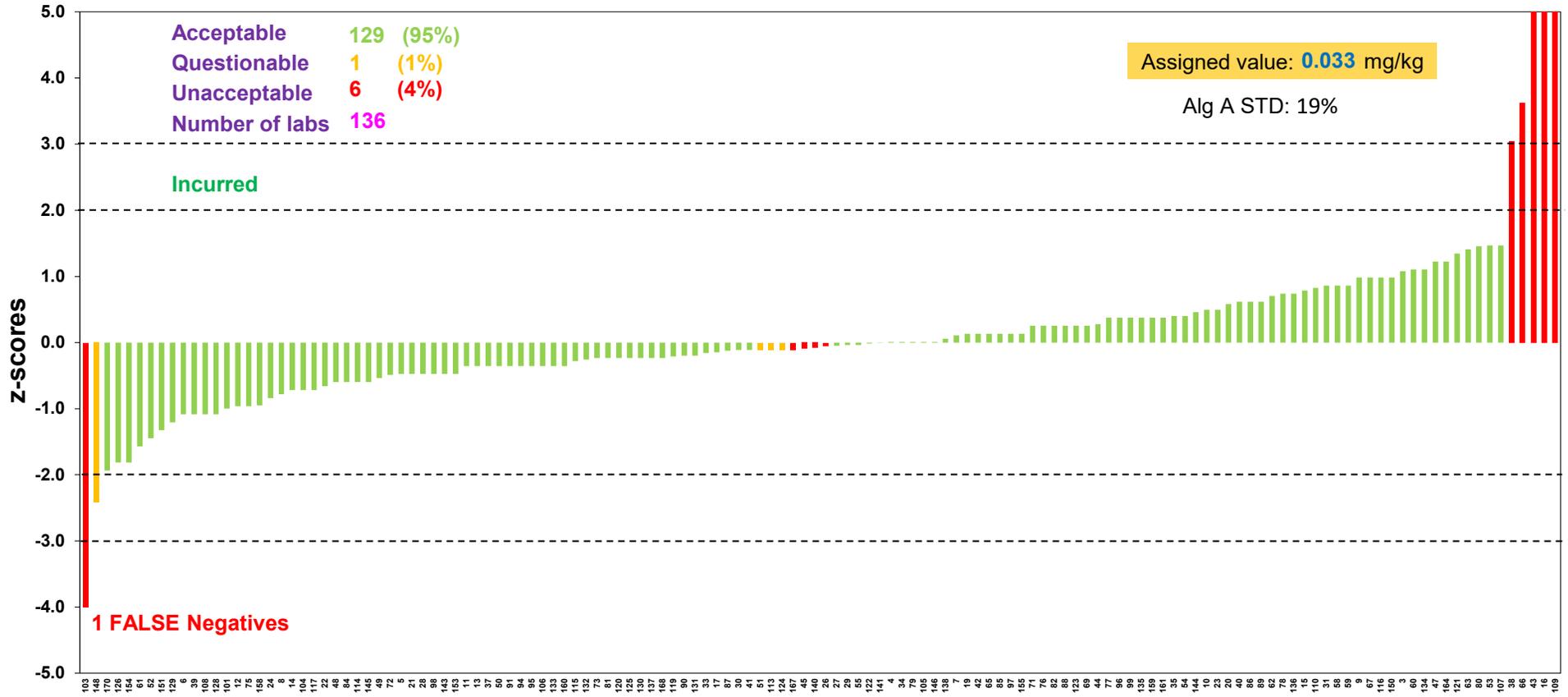
Phenmedipham

EU and EFTA Laboratories



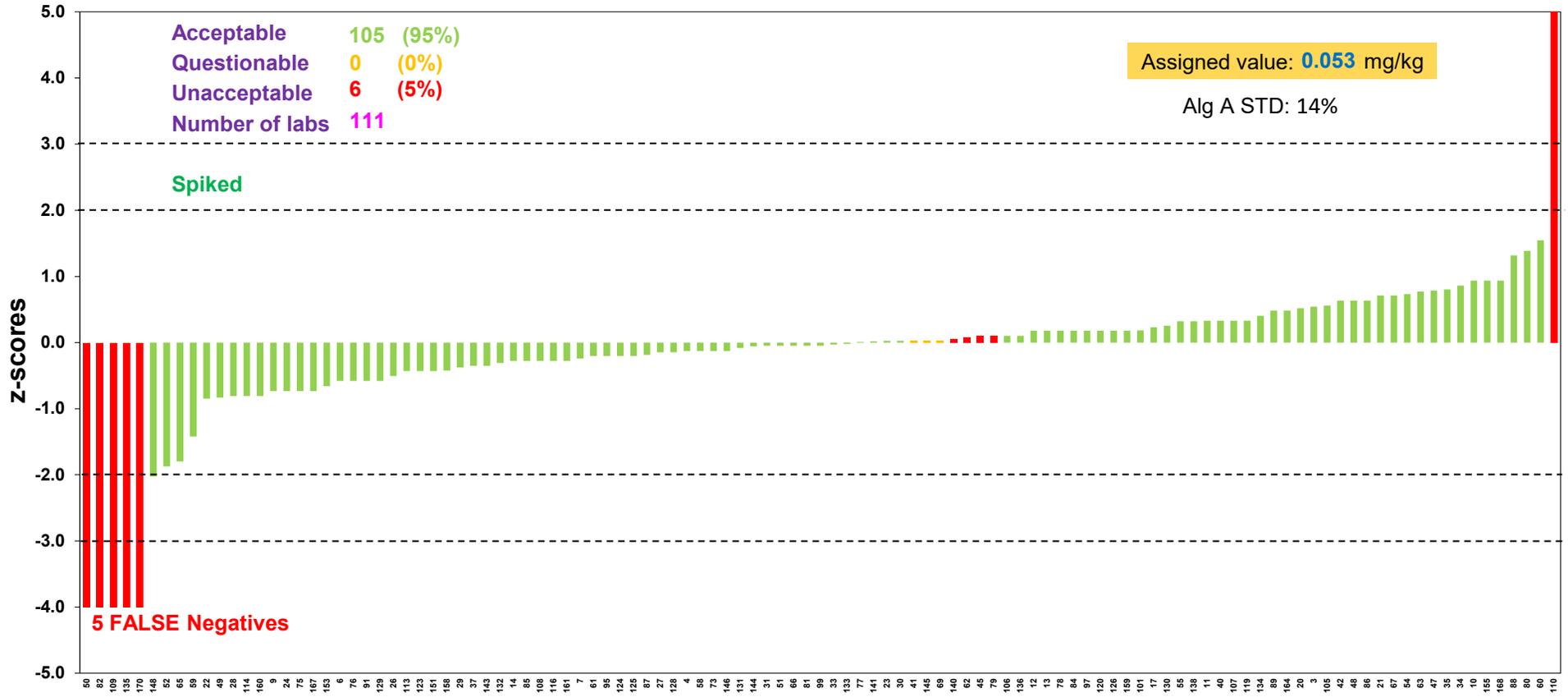
Pirimicarb

EU and EFTA Laboratories



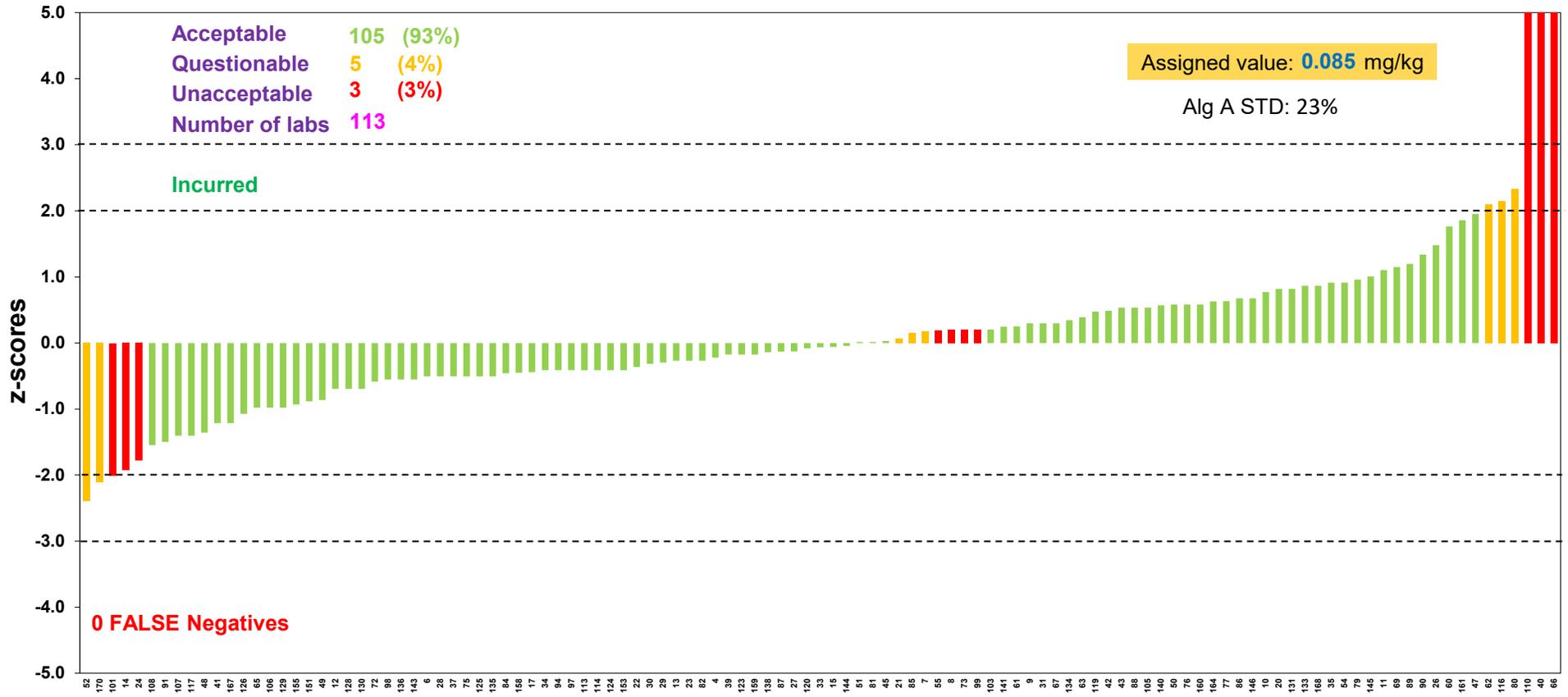
Pirimicarb-desmethyl

EU and EFTA Laboratories

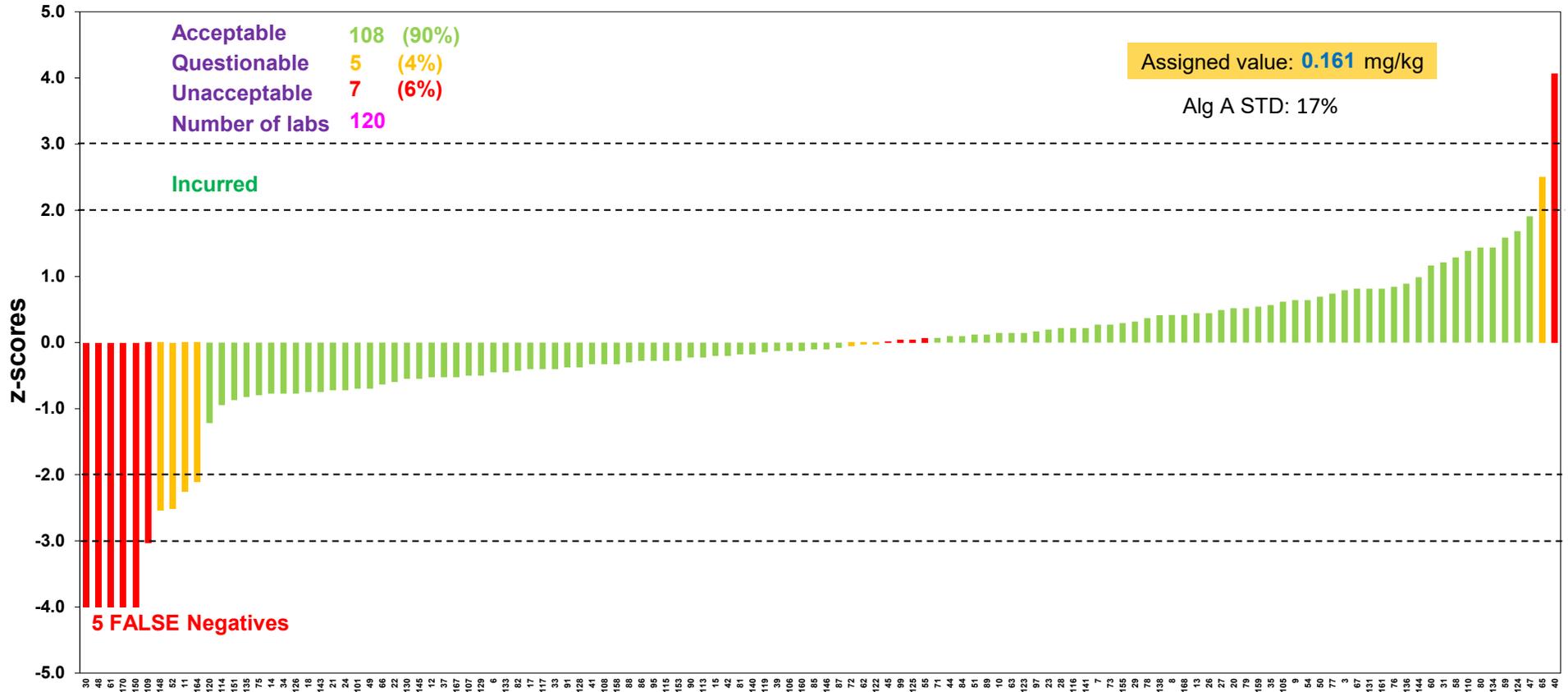


Proquinazid

EU and EFTA Laboratories

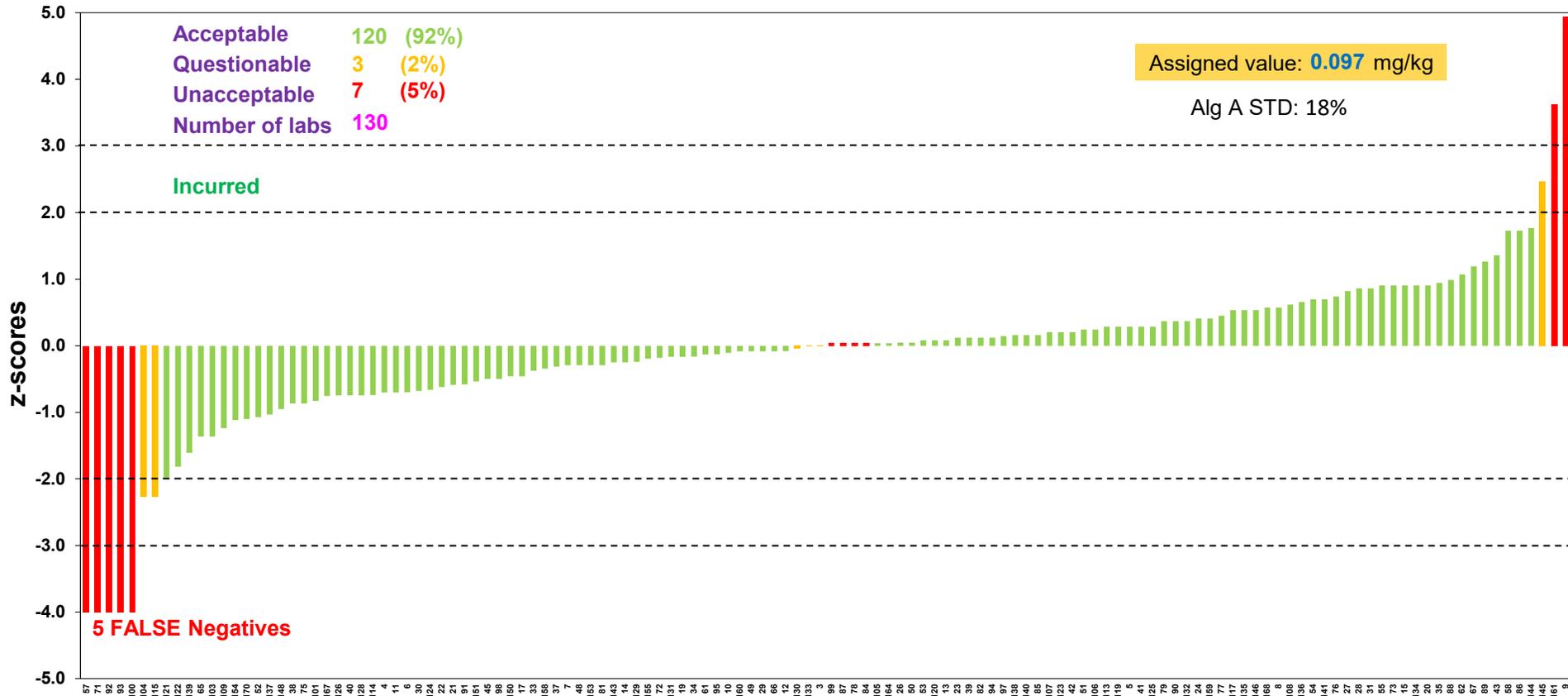


Prothioconazole-desthio EU and EFTA Laboratories



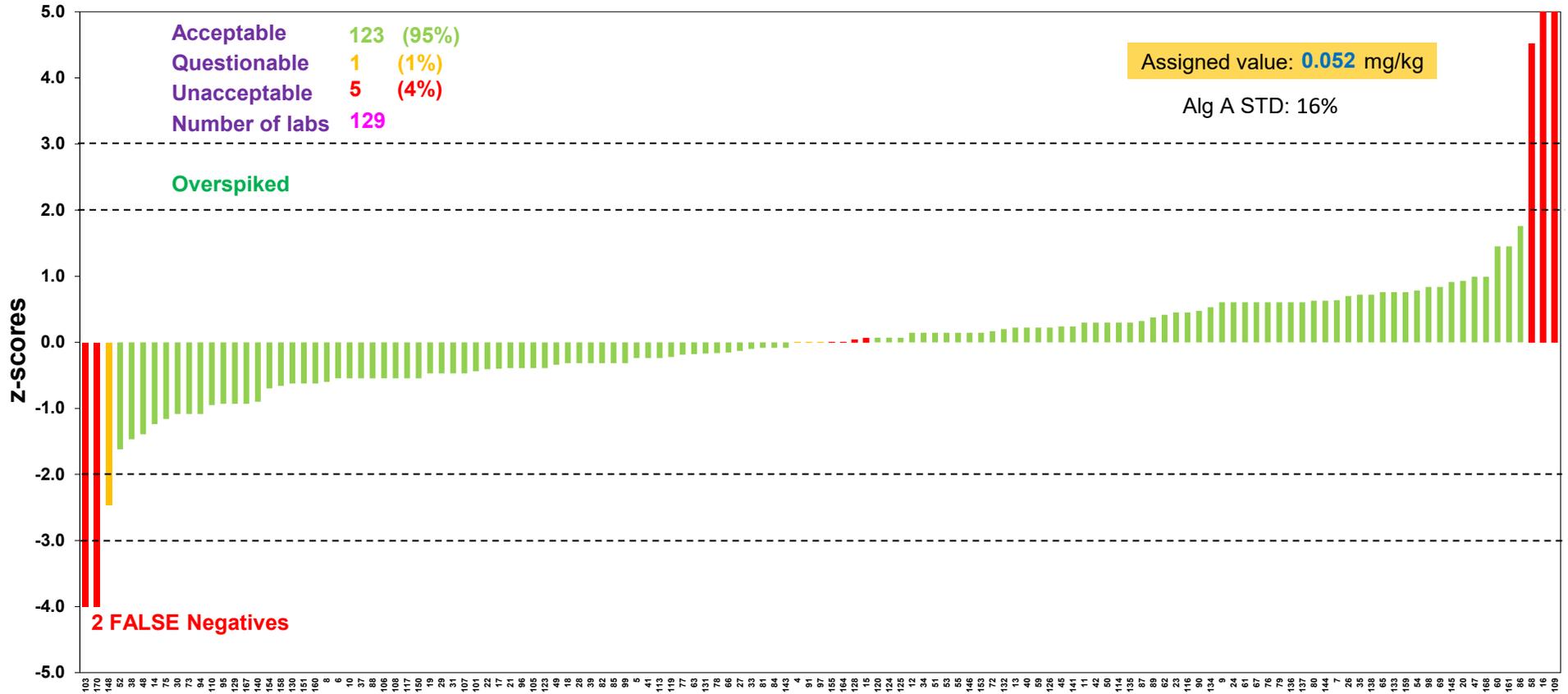
Pyraclostrobin

EU and EFTA Laboratories



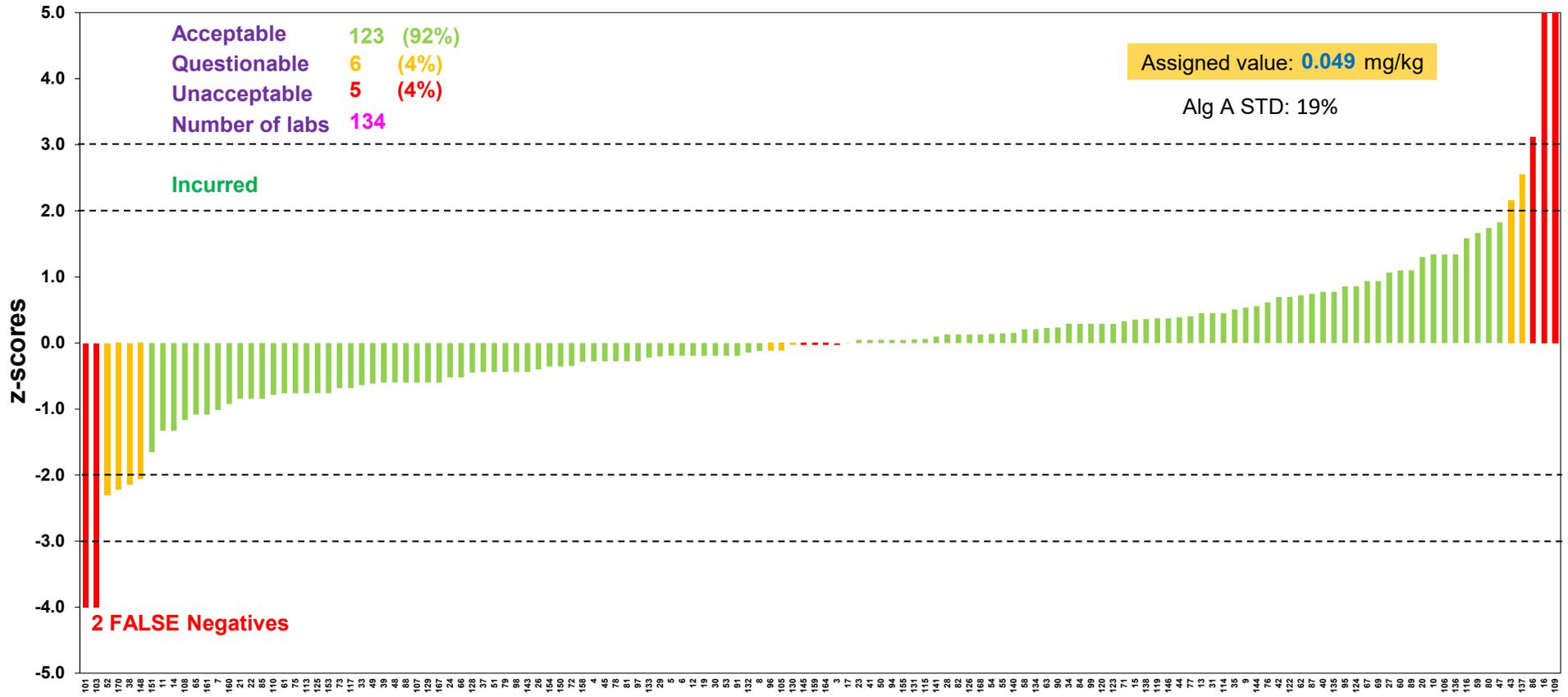
Pyriproxyfen

EU and EFTA Laboratories



Trifloxystrobin

EU and EFTA Laboratories



Calculations of z scores

- For each laboratory/pesticide combination :
- $z = (x-X) / \sigma$
- x is the result reported by the participant or the specific reporting limit of the lab for those labs not having detected the pesticide present in the test material
- X is the assigned value, Alg A mean without outliers
- σ is the target standard deviation obtained by multiplying the median by the FFP RSD of 25%
- $|z| \leq 2$ Acceptable
- $2 < |z| < 3$ Questionable
- $|z| \geq 3$ Unacceptable

Category A laboratories

- To be classified as Category A laboratory the labs had to 1) be able to analyse for at least 90% of the compulsory pesticides on the target pesticides list, 2) have correctly detected and quantified at least 90% of the pesticide present in the test material (7 \geq pesticide residues) and 3) report no false positive.
- Evaluation of the overall performance, the Average of the Squared z-Score (AZ²) are calculated:

$$AZ^2 = \frac{\sum_{i=1}^n Z_i^2}{n}$$

- $z \leq 2$ Good
- $2 < z < 3$ Satisfactory
- $z \geq 3$ Unsatisfactory

