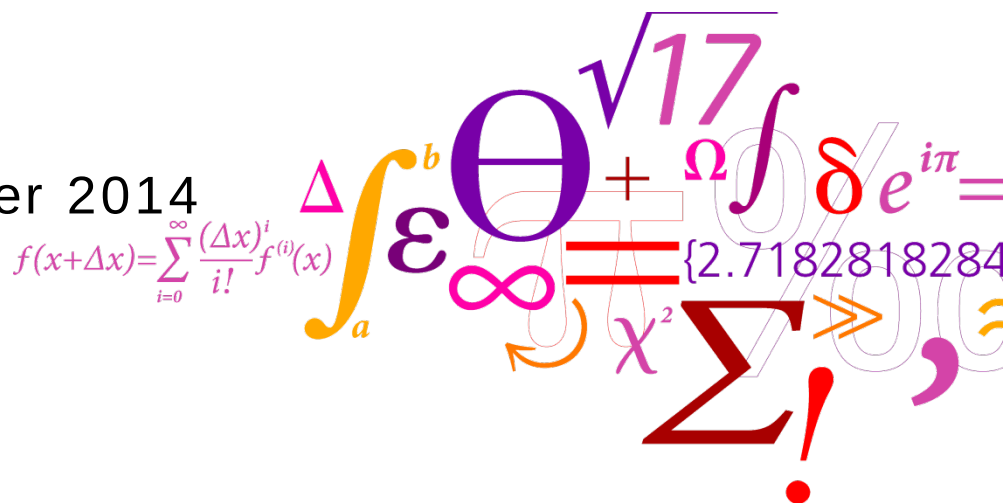


EUPT-CF8

Incurred and spiked pesticides in wheat

Mette Erecius Poulsen, Gitte Andersen and
Susan Strange Herrmann

Copenhagen, 18 December 2014



PTs on cereals / feed – overview

		2007 EUP-T-C1 /SRM2	2008 EUP-T-C2	2009 EUP-T-C3 /SRM4	2010 EUP-T-C4	2011 EUP-T-C5 /SRM6	2012 EUP-T-C6	2013 EUP-T-CF7	2014 EUP-T-CF8
	Test material	Wheat flour	Wheat flour	Oat flour	Rye flour	Rice flour	Barley	Feed	Wheat flour
	no. of participants	64	74	111	118	155 (133)	149 (127)	120 (106)	160 (141)
	No. of target pesticides	37	55	60	72	104	107	116	111
MRM	no. of incurred pesticides	3	9	14	13	10	8	19	14
	no. of spiked pesticides	4	4		3	7	10	4	5
SRM	no. of incurred pesticides	2	2	2	2				
	no. of spiked pesticides	1		2	1	7			
	Total no. of pesticides in test item	10	15	18	19	24	18	23	19

Organising team at EURL

- **Mette Erecius Poulsen, Senior Chemist**
- **Anne Kruse Lykkeberg, Senior Chemist**
- **Gitte Andersen, Chemist**
- **Merete B. Ludwigsen, Chemical Technician**
- **Inge Schröder, Chemical Technician**
- **Lisbet Pilhøj, Chemical Technician**
- **Jens-Ole Frimann, System Developer**

Scientific Group

Advisory Group

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André de Kok

Antonio Valverde

Darinka Štajnbaher

Magnus Jezussek

**Michelangelo
Anastassiades**

Miguel Gamón

Ralf Lippold

Dr. Sonja Masselter

Stewart Reynolds

Tuija Pihlström

Quality Group

Antonio Valverde

Stewart Reynolds

Participation

Country	# labs	Country	# labs	Country	# labs
Argentina	3	Germany	23	Poland	15
Austria	2	Greece	3	Portugal	2
Belgium	3	Hungary	4	Republic of Belarus	1
Brasil	5	Iceland	1	Romania	8
Bulgaria	3	India	2	Serbia	2
Burkina Faso	1	Indonesia	1	Singapore	1
Croatia	5	Ireland	1	Slovakia	2
Cyprus	2	Italy	20	Slovenia	3
Czech Republic	3	Kenya	2	Spain	18
Denmark	1	Lithuania	1	Sweden	2
Egypt	1	Luxembourg	1	Tanzania	1
Estonia	1	Netherlands	6	Thailand	1
Finland	1	New Zealand	1	United Kingdom	3
France	6	Norway	1	Total	163

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Burkina Faso	1	Indonesia	1	Singapore	1
Croatia	5	Ireland	1	Slovakia	2
Cyprus	2	Italy	20	Slovenia	3
Czech Republic	3	Kenya	2	Spain	18
Denmark	1	Lithuania	1	Sweden	2
Egypt	1	Luxembourg	1	Tanzania	1
Estonia	1	Netherlands	6	Thailand	1
Finland	1	New Zealand	1	United Kingdom	3
France	6	Norway	1	Total	163

Target Pesticide List

- 111 pesticides
- 4 new
 - Bixafen
 - Flonicamid
 - Fluxapyroxad
 - Metrafenone
- 9 deleted
 - Aldrin
 - Chlordane, cis-
 - Chlordane, oxy
 - Chlordane, trans-
 - Dieldrin
 - Endrin
 - Heptachlor
 - Heptachlorepoxyd-cis
 - Heptachlorepoxyd-trans



TARGET PESTICIDE LIST

for the EUPT-CF8 2014

(last updated: 23.01.2014)

Four new pesticides added to the Target Pesticide List from EUPT-CF7 (2013) are marked in bold.

Nine pesticides are deleted from Target Pesticide List from EUPT-CF7 (2013): aldrin, chlordane, cis-, chlordane, oxy-, chlordane, trans-, dieldrin, endrin, heptachlor, heptachlorepoxyd-cis and heptachlorepoxyd-trans

MRM-Compounds

Pestide no.	Pesticides	MRRL (mg/kg)
1	Acephate	0.01
2	Azinphos-methyl	0.01
3	Azoxystrobin	0.01
4	Bifenthrin	0.01
5	Bixafen	0.01
6	Boscalid	0.01
7	Captan	0.01
8	Carbaryl	0.01

Wheat

- Grown in Denmark in 2013
- Field treated by Aarhus University, Research Department Flakkebjerg

Pesticide	Application on cereals in the field	Spike in laboratory
Azoxystrobin	x	
Bixafen	x	
Boscalid	x	
Carbendazim		x
Chlorothalonil	x	x
Cypermethrin	x	x
Deltamethrin-cis	x	x
Endosulfan-sulfate		x
Epoxiconazole	x	
Flonicamid	x	
Fluxapyroxad	x	
Lindane		x
Linuron		x
Metconazole	x	
Metrafenone	x	x
Prothioconazole	x	
Pyraclostrobin	x	
Spiroxamine	x	x
Trifluralin		x





Sp











Sample shipment

- Samples were distributed on Monday 19 May 2014 (13 May to Third Countries)
- Most samples were delivered to EU laboratories on 20 or 21 May 2014



Homogeneity test

	Mean, mg/kg	S_s^2	c	$S_s^2 < c$
Azoxystrobin	0.211	0.00000	0.0033	Pass
Bixafen	0.082	0.00005	0.0001	Pass
Boscalid	0.324	0	0.0063	Pass
Carbendazim	0.055	0.00001	0.0001	Pass
Chlorthalonil	0.029	0.00001	0.0001	Pass
Cypermethrin	0.891	0	0.0482	Pass
Deltamethrin	0.053	0	0.0002	Pass
Endosulfan-sulfate	0.057	0	0.0002	Pass
Epoxiconazole	0.122	0	0.0008	Pass
Flonicamid	0.102	0	0.0003	Pass
Fluxapyroxade	0.179	0.00017	0.0004	Pass
Lindane	0.035	0	0.0000	Pass
Linuron	0.069	0.00002	0.0003	Pass
Metconazole	0.110	0.00014	0.0001	Pass
Metrafenone	0.381	0	0.0081	Pass
Prothioconazole desthio	0.179	0.00040	0.0004	Pass
Pyraclostrobin	0.070	0.00004	0.0001	Pass
Spiroxamin	0.064	0.00006	0.0001	Pass
Trifluralin	0.058	0	0.0001	Pass

Stability test

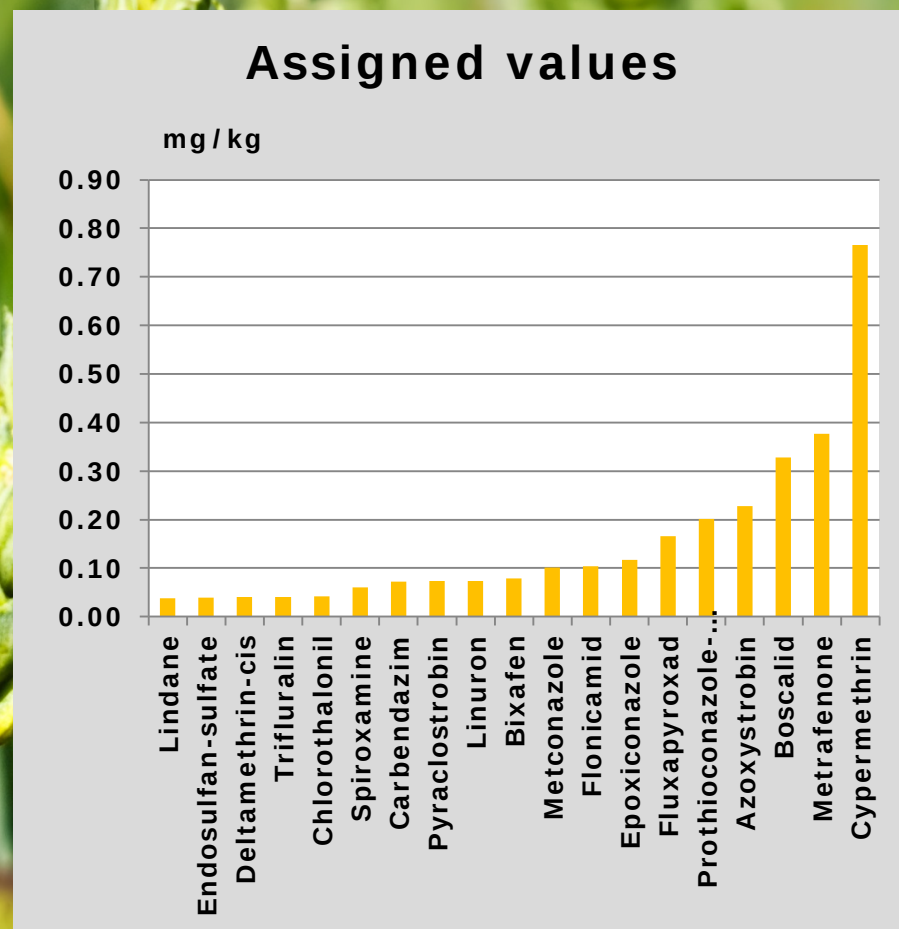
	Mean, mg/kg	Freezer $ x_1 - y_i $	$0.3 \times \sigma$	$ x_1 - y_i \leq 0.3 \times \sigma$
Azoxystrobin	0.243	0.017	0.017	Pass
Bixafen	0.071	0.001	0.006	Pass
Boscalid	0.305	0.015	0.025	Pass
Carbendazim	0.058	0.000	0.000	Pass
Chlorothalonil	0.027	0.003	0.003	Pass
Cypermethrin	0.908	0.053	0.057	Pass
Deltamethrin	0.042	0.003	0.003	Pass
Endosulfan-sulfate	0.034	0.000	0.003	Pass
Epoxiconazole	0.118	0.005	0.009	Pass
Flonicamid	0.088	0.004	0.008	Pass
Fluxapyroxade	0.150	0.012	0.012	Pass
Lindane	0.038	0.003	0.003	Pass
Linuron	0.065	0.004	0.006	Pass
Metconazole	0.098	0.005	0.008	Pass
Metrafenone	0.362	0.015	0.028	Pass
Prothioconazole-desthio	0.159	0.005	0.015	Pass
Pyraclostrobin	0.061	0.004	0.006	Pass
Spiroxamin	0.057	0.003	0.005	Pass
Trifluralin	0.034	0.002	0.003	Pass

Calculation of assigned values and uncertainty of assigned values

- Algorithm A mean of the results from EU laboratories (and EFTA)
 - Only result from participant that
 - Reported to add water to the samples before extraction or
 - used mixture of solvent and water or
 - used ASE
- Outliers
 - Only obvious uncorrect results
- Uncertainty
 - $u = 1.25 * (s^* / \sqrt{n})$
 - s^* is robust standard deviation (Alg A standard deviation)
 - N is the number of participants

Assigned values

PESTICIDES	Assigned values only water addition, mg/kg
Azoxystrobin	0.228
Bixafen	0.079
Boscalid	0.328
Carbendazim	0.073
Chlorothalonil	0.042
Cypermethrin	0.766
Deltamethrin-cis	0.040
Endosulfan-sulfate	0.040
Epoxiconazole	0.117
Flonicamid	0.104
Fluxapyroxad	0.165
Lindane	0.038
Linuron	0.074
Metconazole	0.101
Metrafenone	0.376
Prothioconazole-desthio	0.201
Pyraclostrobin	0.074
Spiroxamine	0.060
Trifluralin	0.040



Pesticide	No. of reported results	No. of NA	False negatives	% results
Azoxystrobin	116	19	2	85
Bixafen	67	68	0	49
Boscalid	117	18	1	86
Carbendazim	97	38	1	71
Chlorothalonil	90	45	22	66
Cypermethrin	125	10	1	92
Deltamethrin-cis	123	12	10	90
Endosulfan-sulfate	126	9	7	93
Epoxiconazole	110	25	1	81
Flonicamid	79	56	0	58
Fluxapyroxad	60	75	3	44
Lindane	126	10	5	93
Linuron	95	40	2	70
Metconazole	87	48	2	64
Metrafenone	83	52	1	61
Prothioconazole-desthio	86	49	3	63
Pyraclostrobin	97	38	2	71
Spiroxamine	97	38	4	71
Trifluralin	106	29	2	78

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False positive results

Lab code	Pesticide	Concentration mg/kg	Determination technique	RL, mg/kg
104	Captan	0.209	LC-MS/MS QQQ	0.06
1	Fenvalerate and Esfenvalerate	0.01	GC-Ion Trap	0.01
147	HCH-beta	0.0294	GC-MS/MS (QQQ)	0.01
111	Quinoxifen	0.01		
75 *	Permethrin	0.0946	GC- (μ) ECD	0.005
69 *	Tebuconazole	0.057	LC-MS/MS QQQ	0.01

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 |
| • $2 < z \leq 3$ | Questionable |
| • $ z > 3$ | Unacceptable |

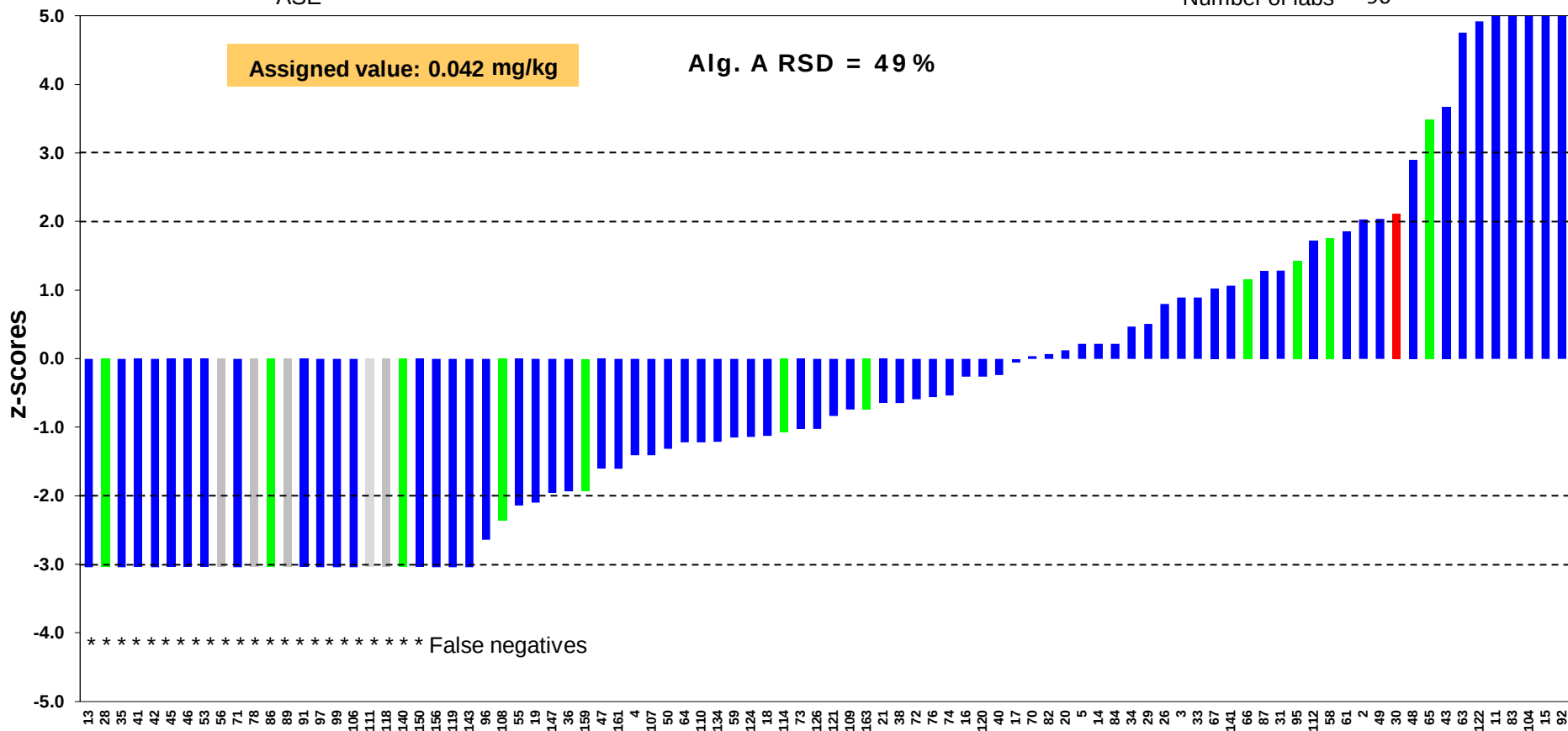
- Water added
- No water added
- Not specified
- ASE

Chlorothalonil

Acceptable 51 (56%)
Questionable 30 (34%)
Unacceptable 9 (10%)
Number of labs 90

Assigned value: 0.042 mg/kg

Alg. A RSD = 49 %



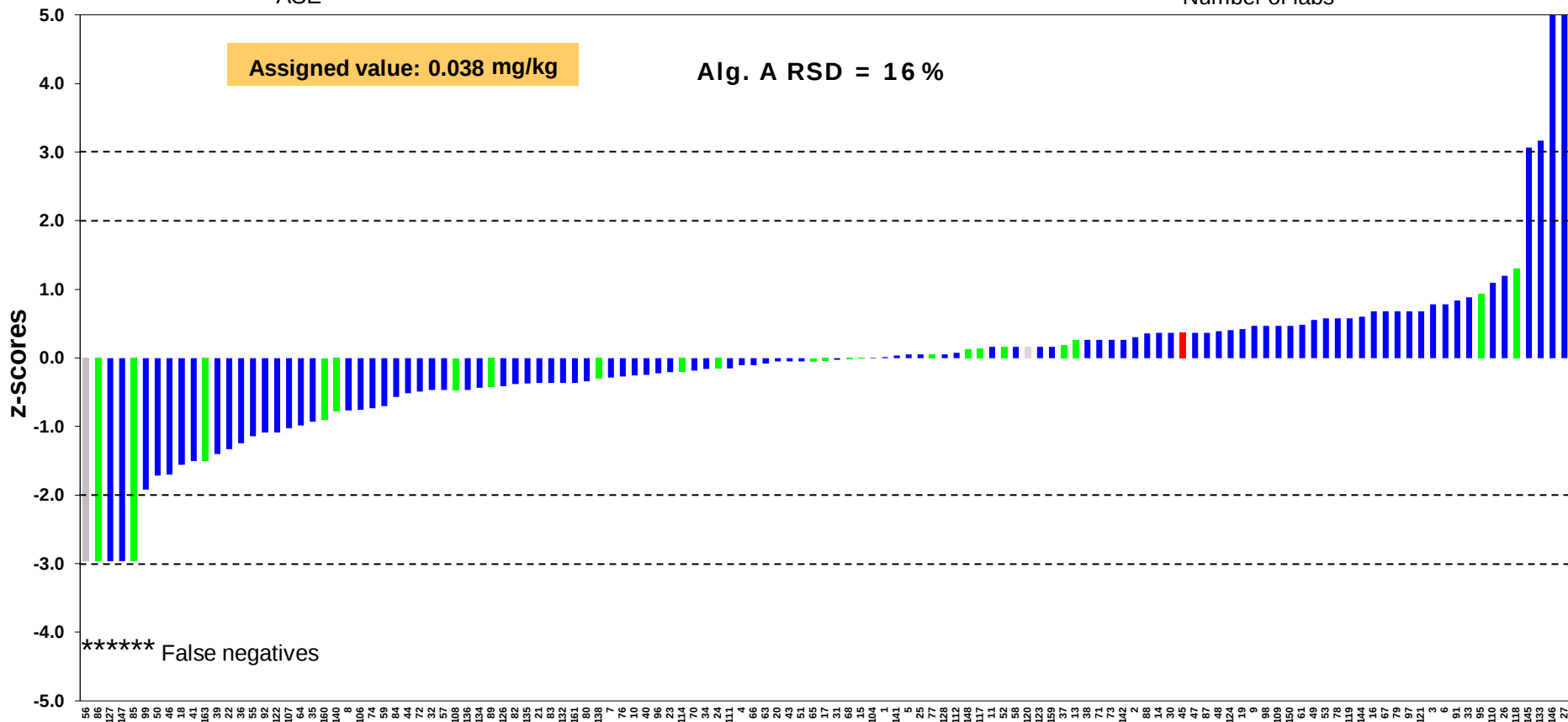
- Water added
- No water added
- Not specified
- ASE

Lindane

Acceptable 112 (90%)
Questionable 9 (7%)
Unacceptable 4 (3%)
Number of labs 125

Assigned value: 0.038 mg/kg

Alg. A RSD = 16 %

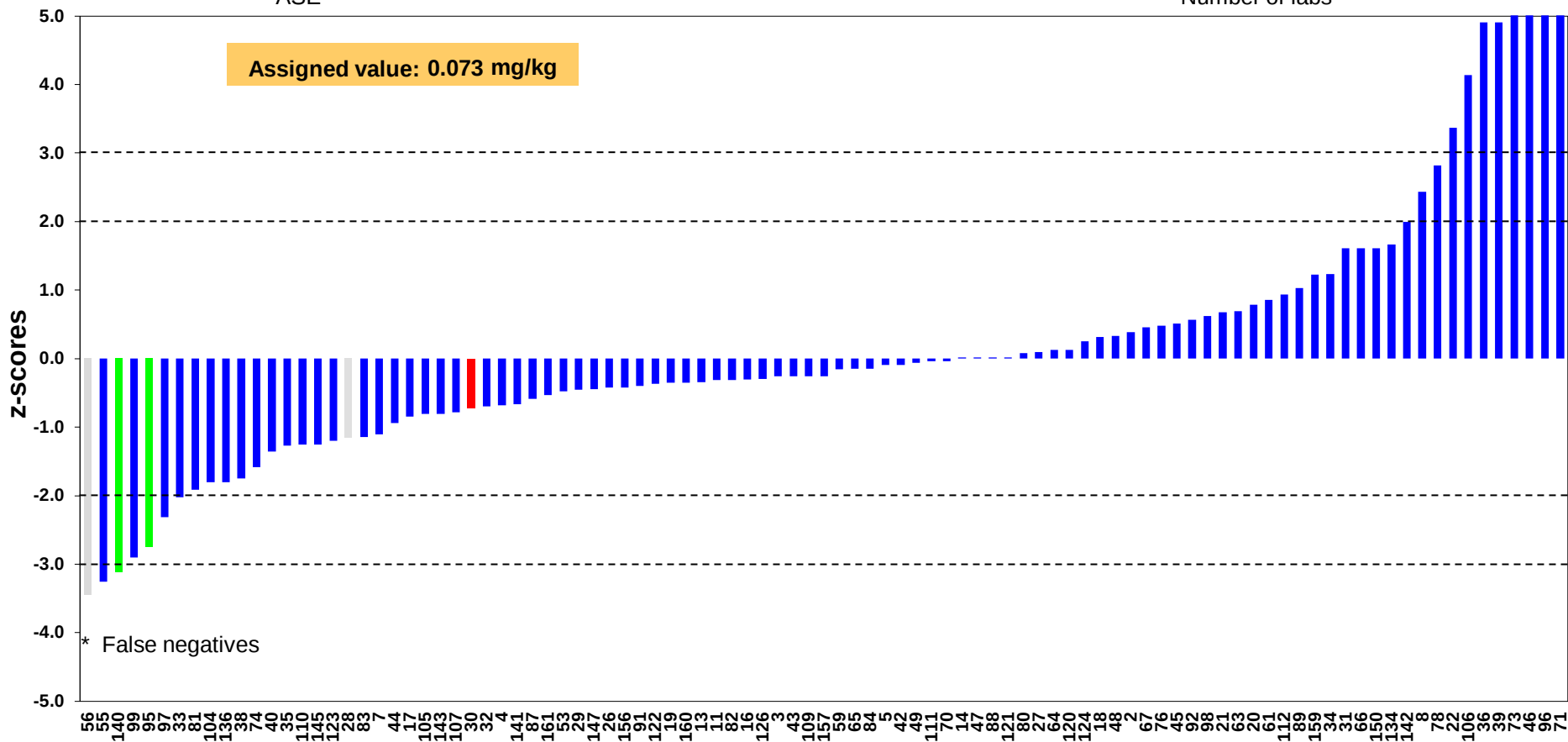


- Water added
- No water added
- Not specified
- ASE

Carbendazim

Acceptable 81 (84%)
 Questionable 5 (4%)
 Unacceptable 11 (12%)
 Number of labs 97

Assigned value: 0.073 mg/kg



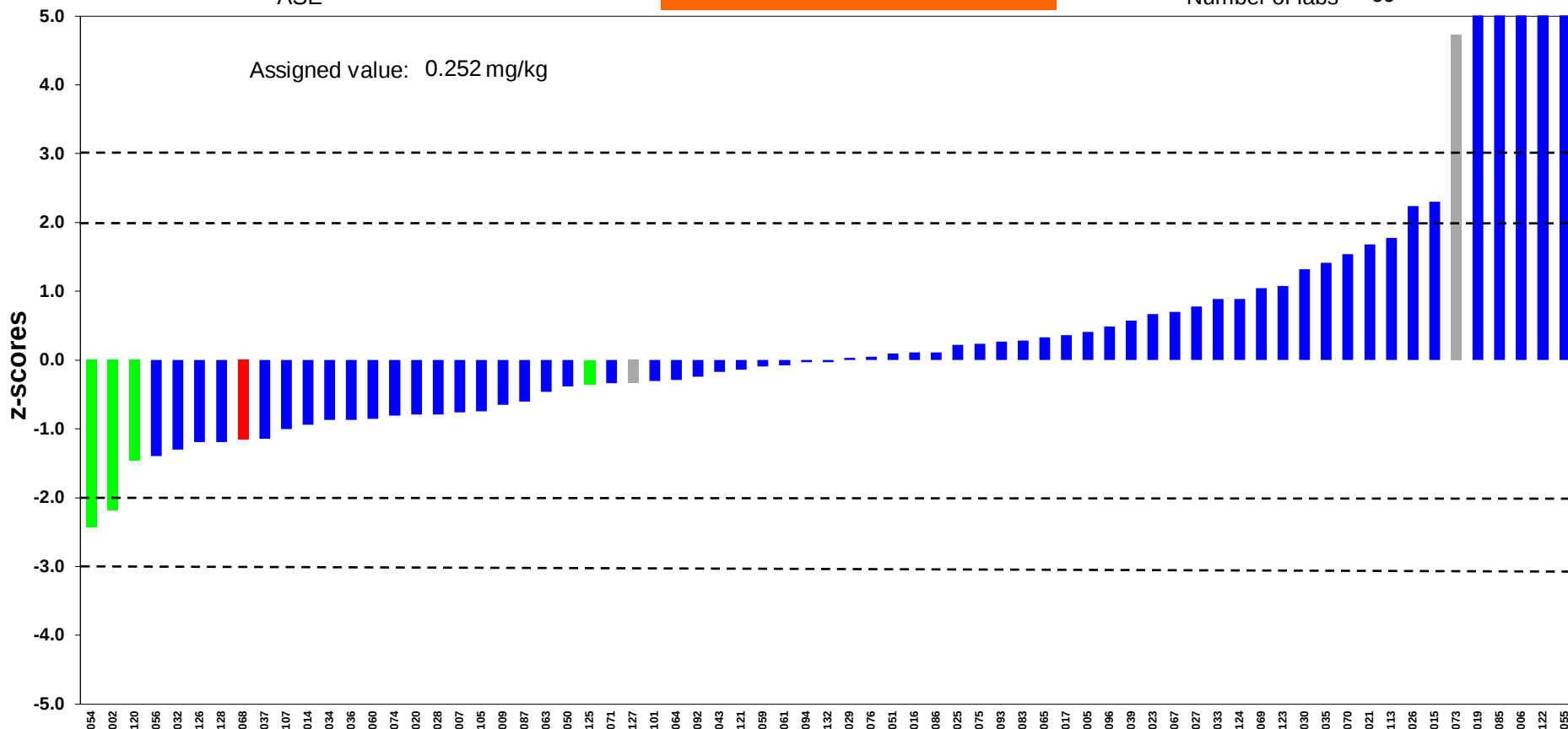
- Water added
- No water added
- Not specified
- ASE

Carbendazim

EUPT-CF7

Acceptable 59
Questionable 4
Unacceptable 6
Number of labs 69

Assigned value: 0.252 mg/kg



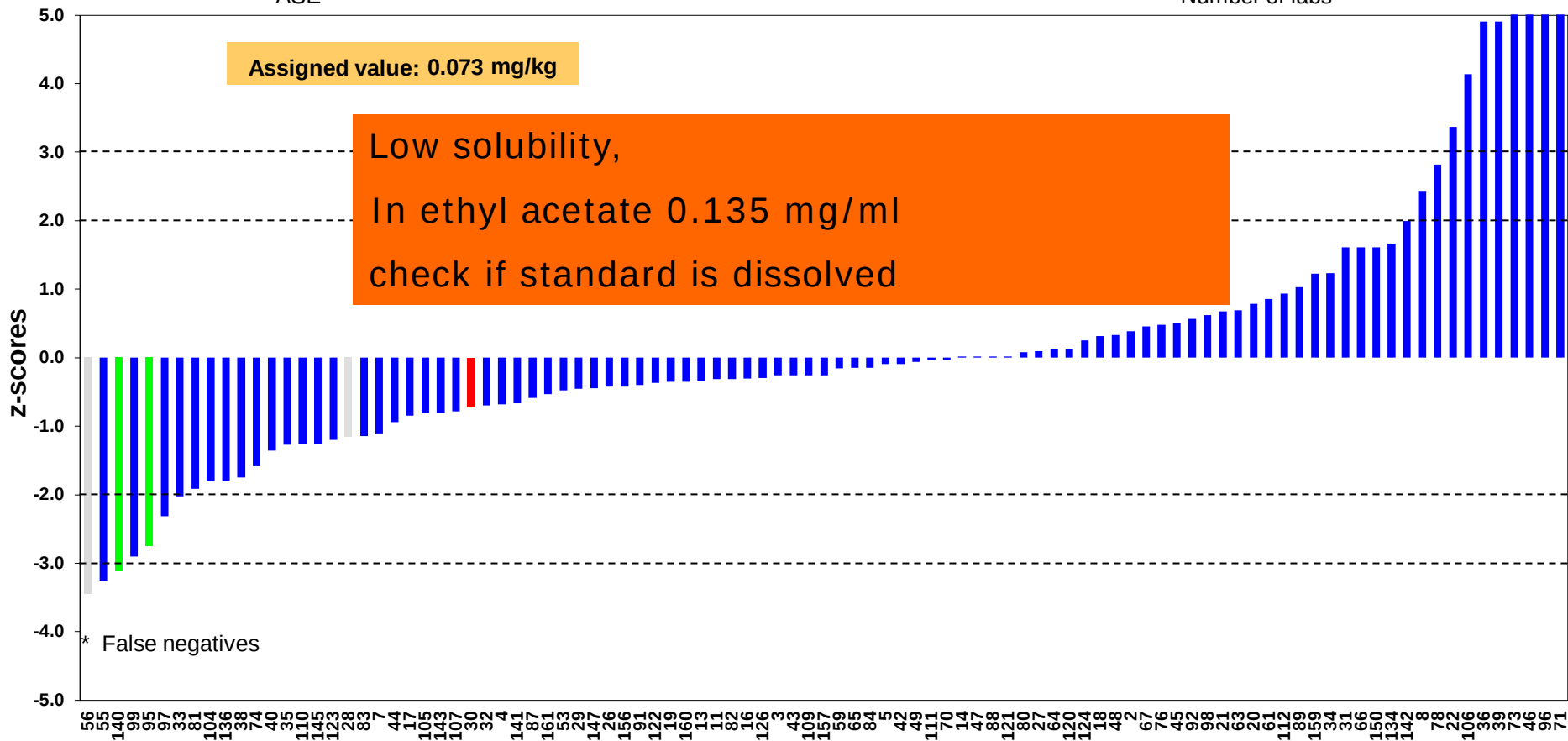
- Water added
- No water added
- Not specified
- ASE

Carbendazim

Acceptable	81	(84%)
Questionable	5	(4%)
Unacceptable	11	(12%)
Number of labs	97	

Assigned value: 0.073 mg/kg

Low solubility,
In ethyl acetate 0.135 mg/ml
check if standard is dissolved

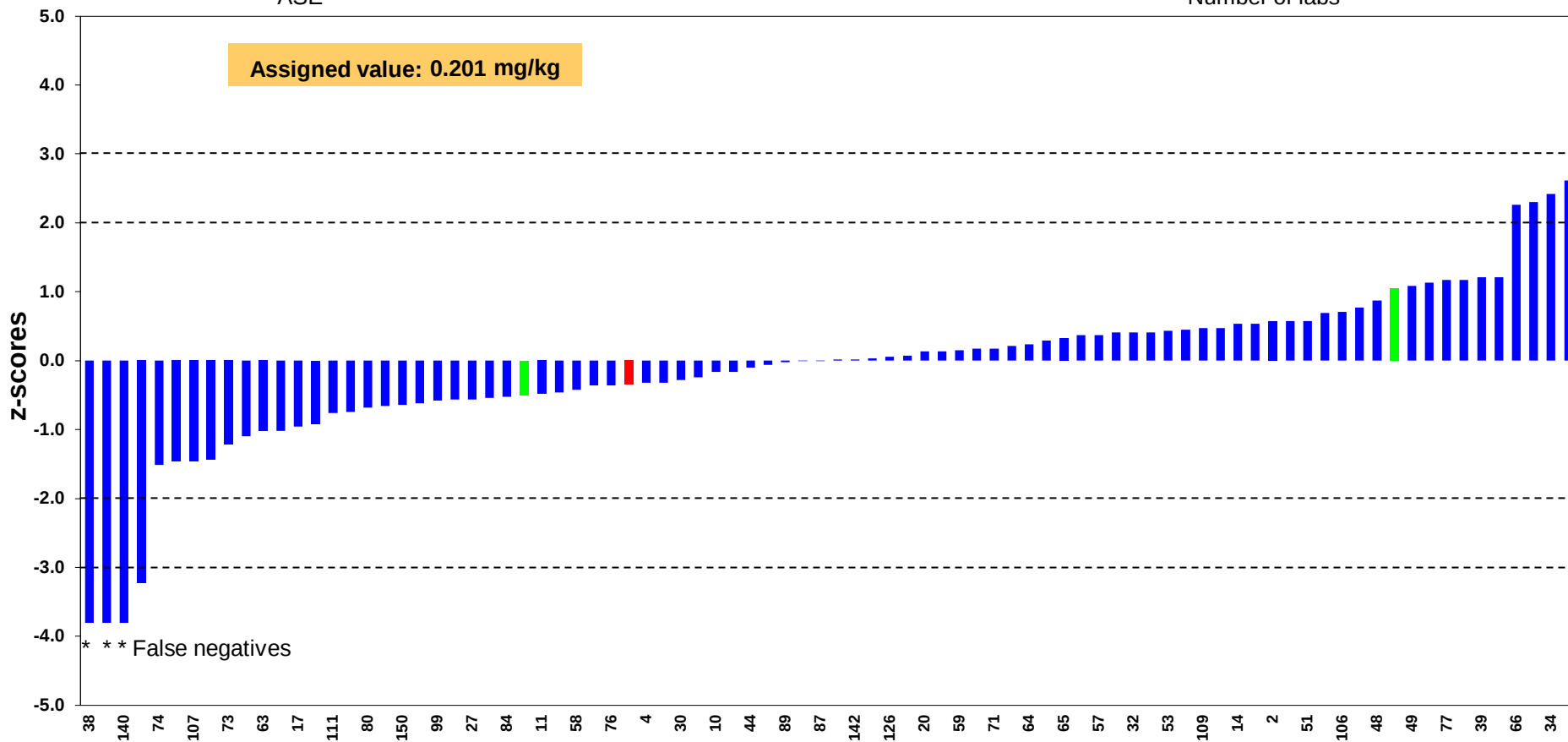


- Water added
- No water added
- Not specified
- ASE

Prothioconazole-desthio

Acceptable	78	(91%)
Questionable	4	(5%)
Unacceptable	4	(5%)
Number of labs	86	

Assigned value: 0.201 mg/kg

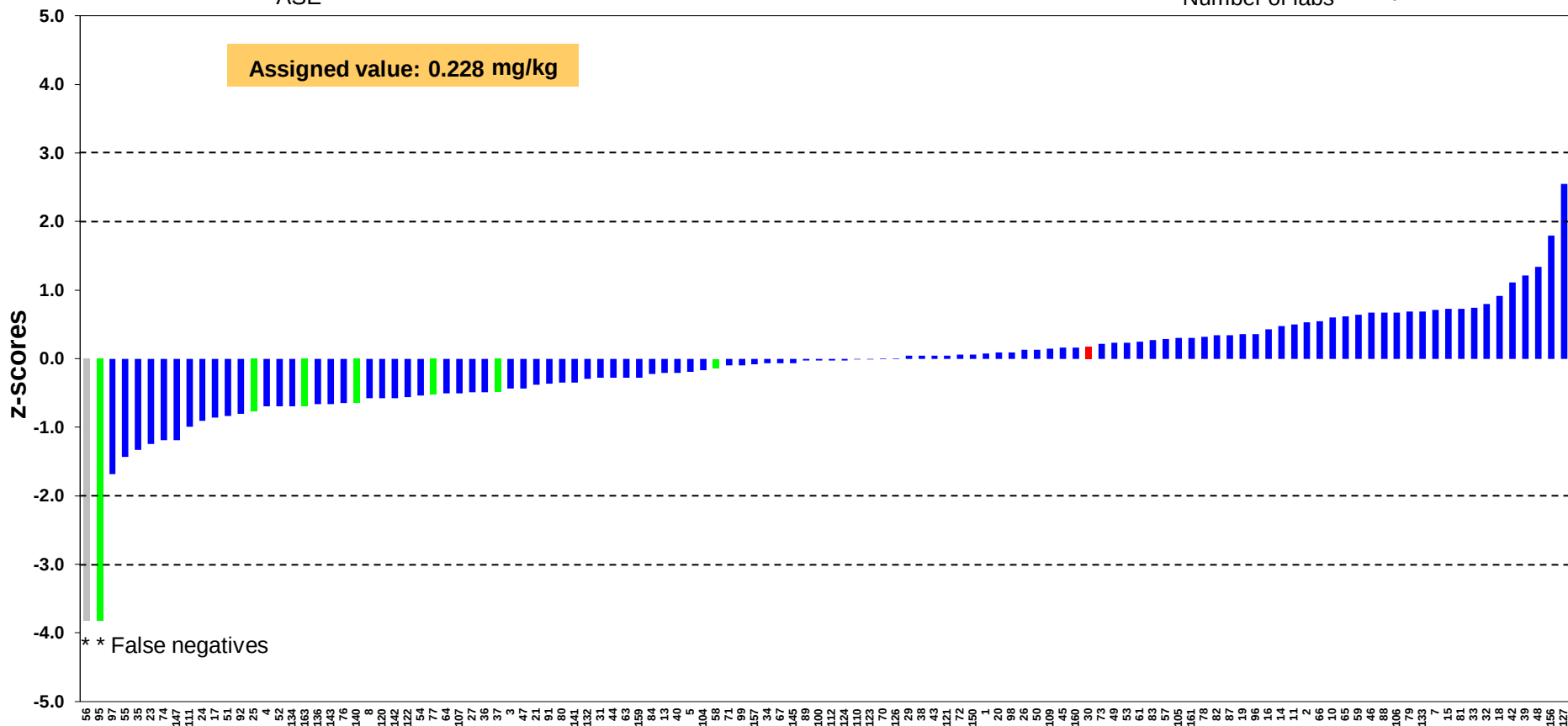


- Water added
- No water added
- Not specified
- ASE

Azoxystrobin

Acceptable	113	(97%)
Questionable	1	(1%)
Unacceptable	2	(2%)
Number of labs	116	

Assigned value: 0.228 mg/kg

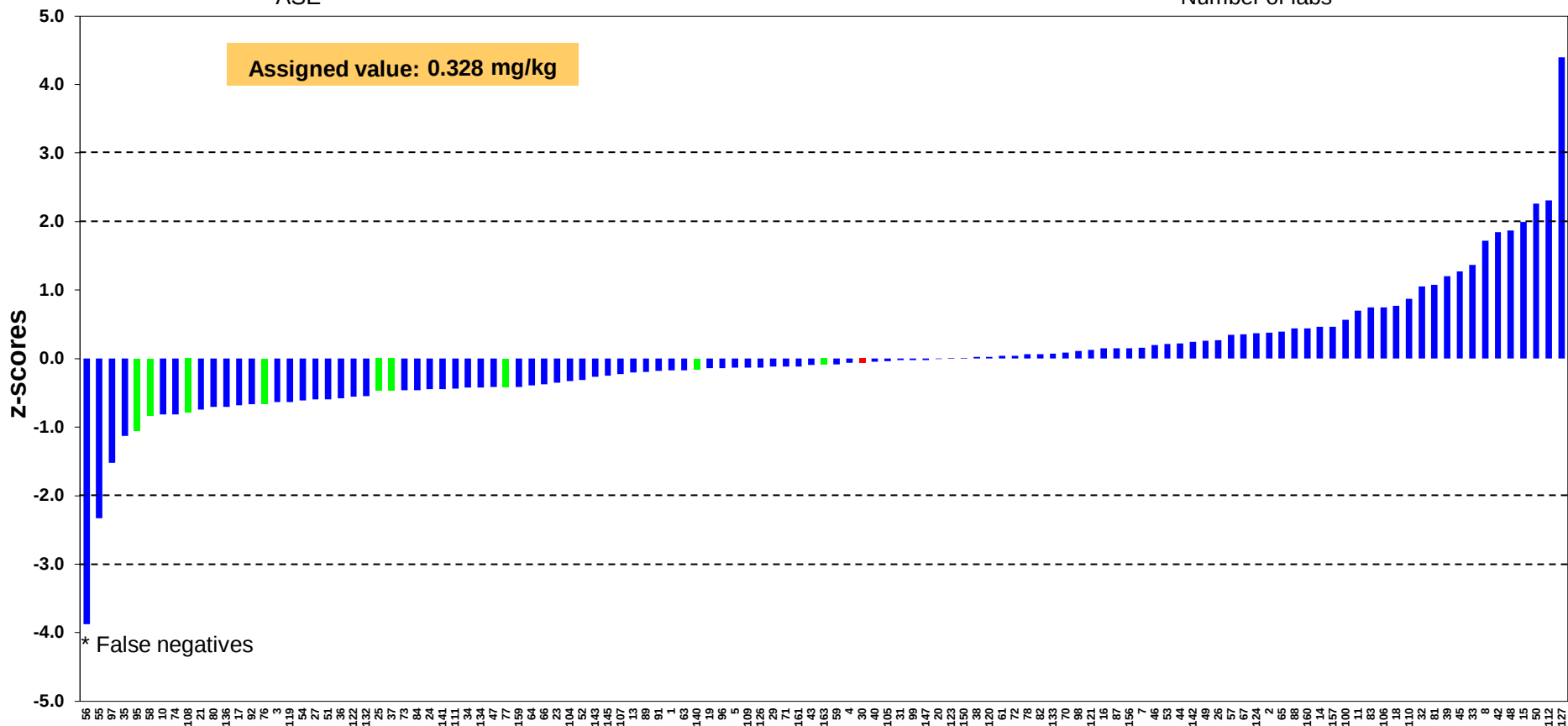


- Water added
- No water added
- Not specified
- ASE

Boscalid

Acceptable 112 (97%)
Questionable 3 (1%)
Unacceptable 2 (2%)
Number of labs 117

Assigned value: 0.328 mg/kg

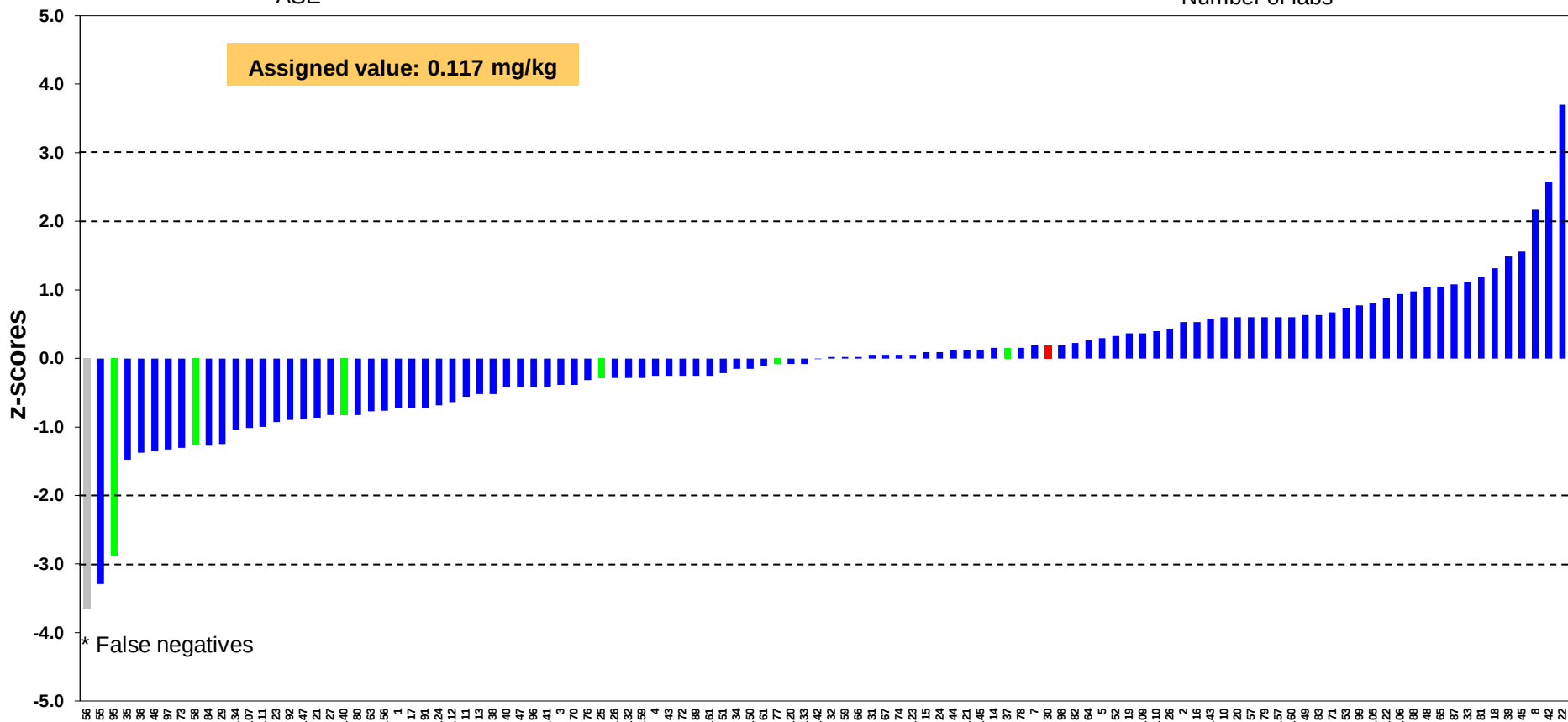


- Water added
- No water added
- Not specified
- ASE

Epoxiconazole

Acceptable	104	(95%)
Questionable	3	(3%)
Unacceptable	3	(2%)
Number of labs	110	

Assigned value: 0.117 mg/kg

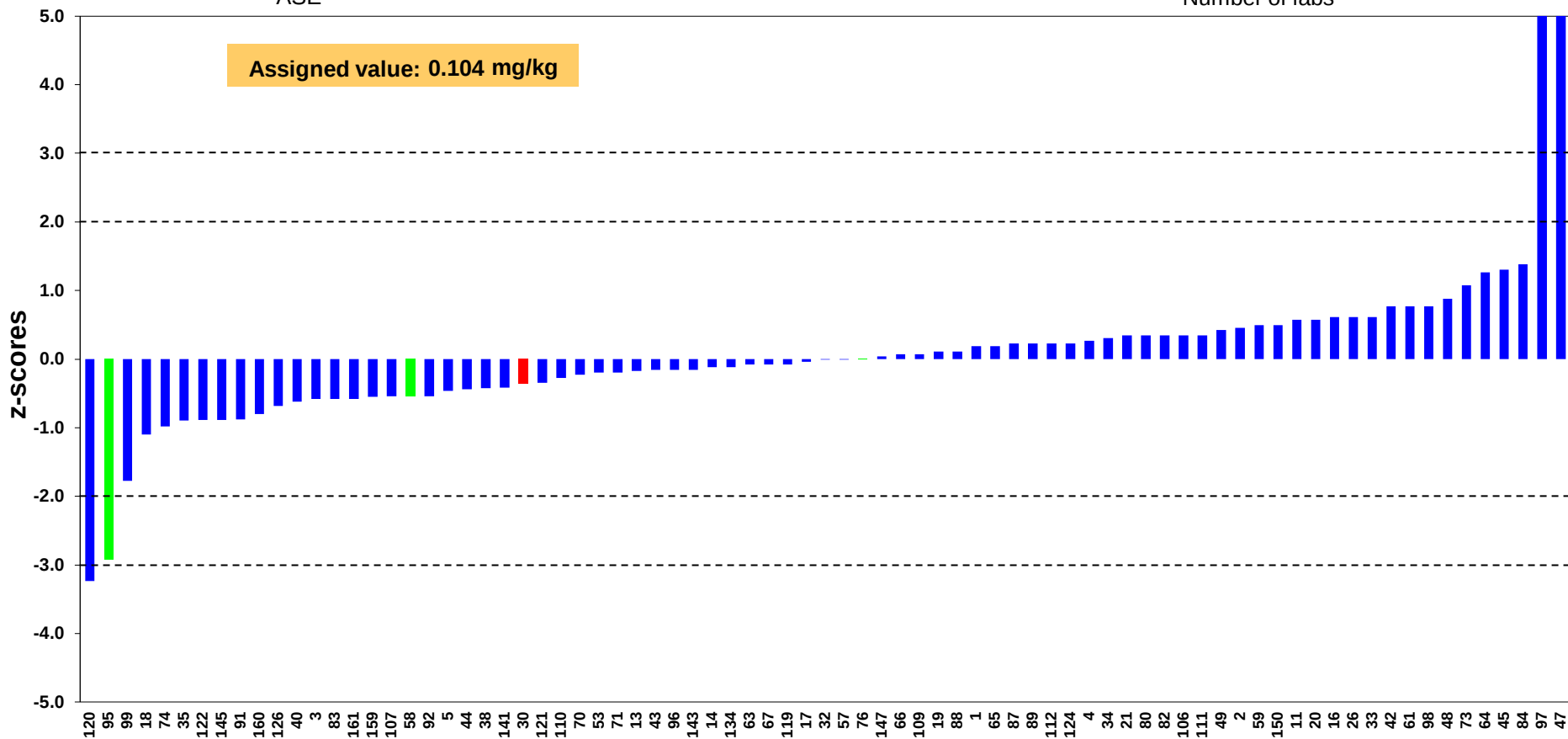


- Water added
- No water added
- Not specified
- ASE

Flonicamid

Acceptable	75	(96%)
Questionable	1	(0%)
Unacceptable	3	(4%)
Number of labs	79	

Assigned value: 0.104 mg/kg

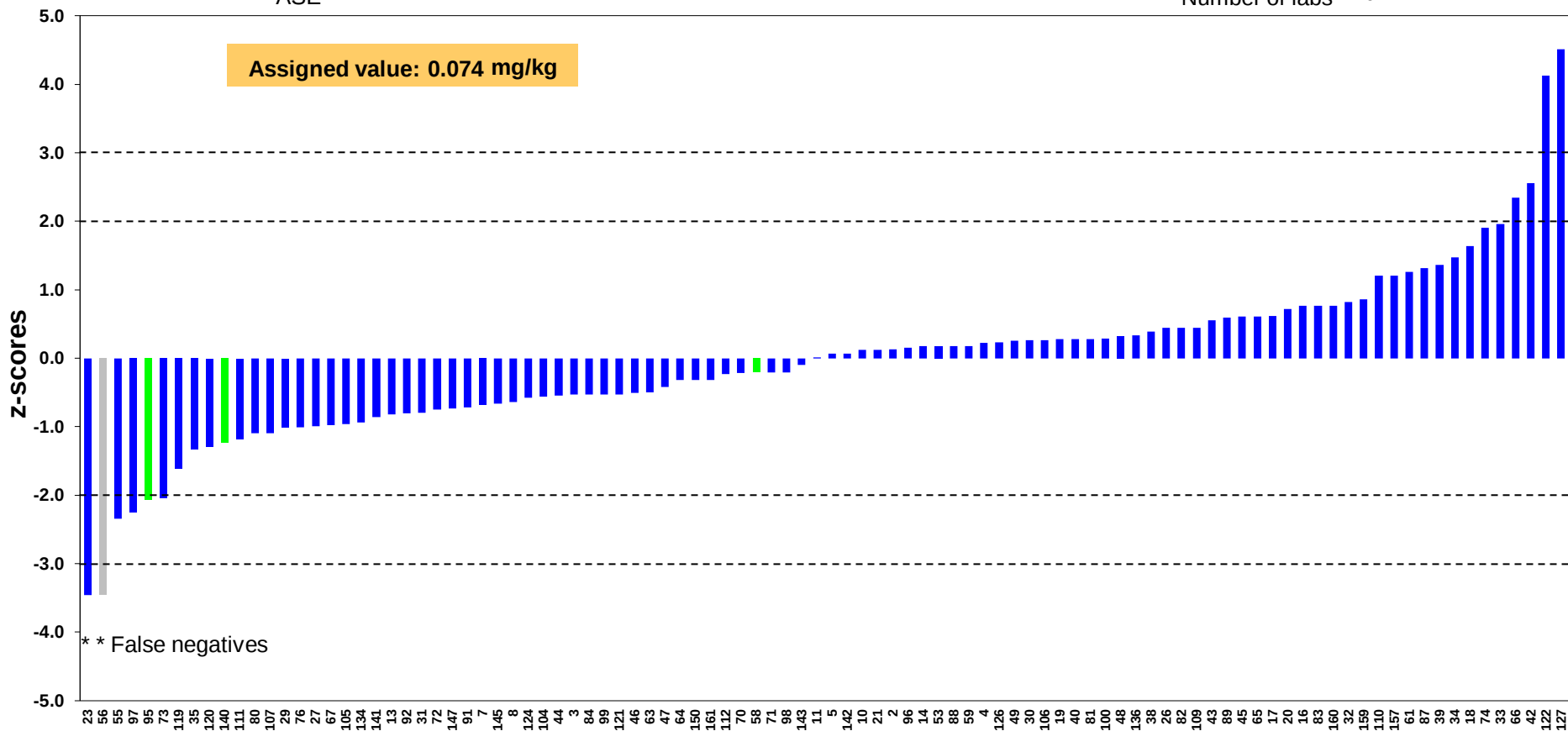


- Water added
- No water added
- Not specified
- ASE

Pyraclostrobin

Acceptable	89	(92%)
Questionable	4	(4%)
Unacceptable	4	(4%)
Number of labs	97	

Assigned value: 0.074 mg/kg

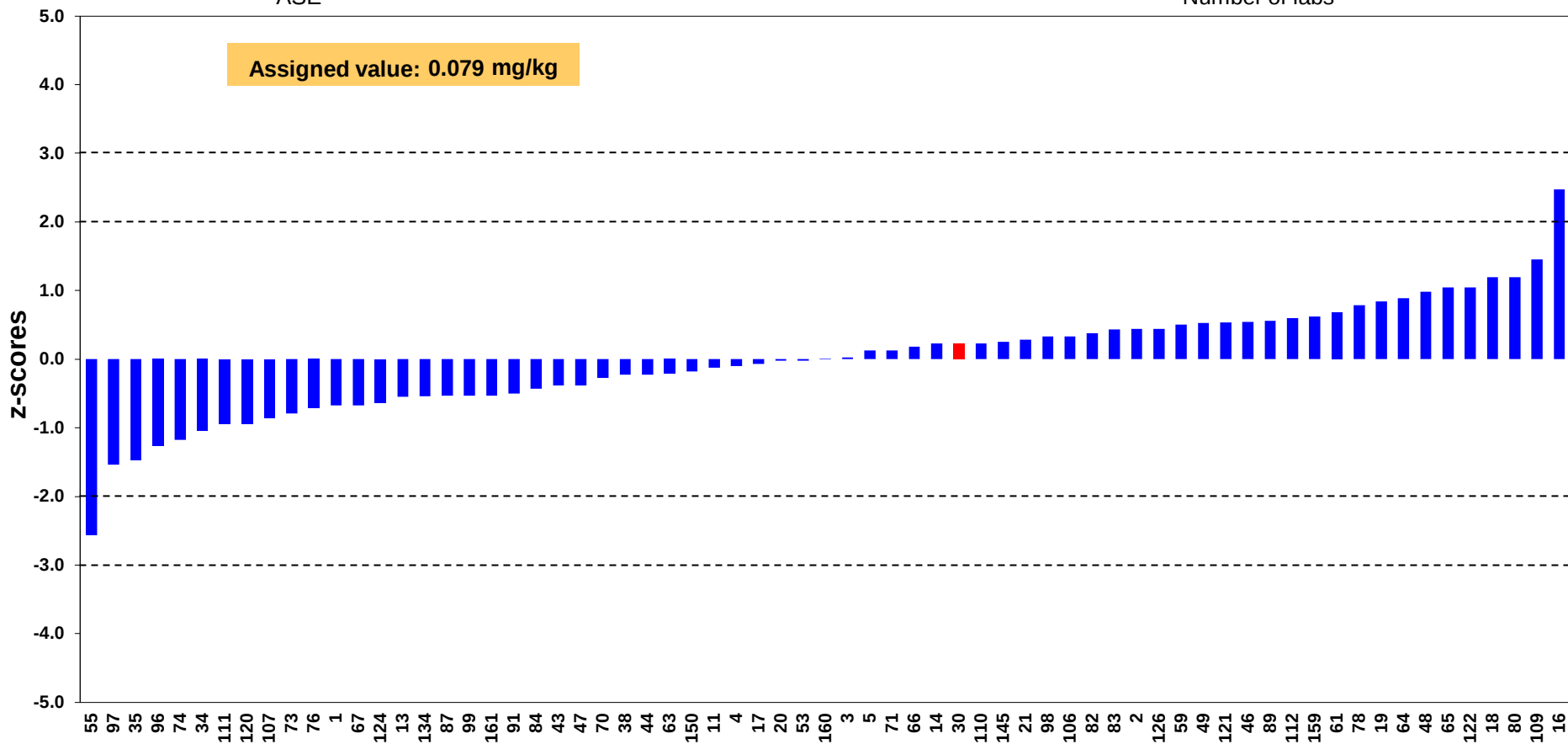


- Water added
- No water added
- Not specified
- ASE

Bixafen

Acceptable	65	(97%)
Questionable	2	(3%)
Unacceptable	0	(0%)
Number of labs	67	

Assigned value: 0.079 mg/kg

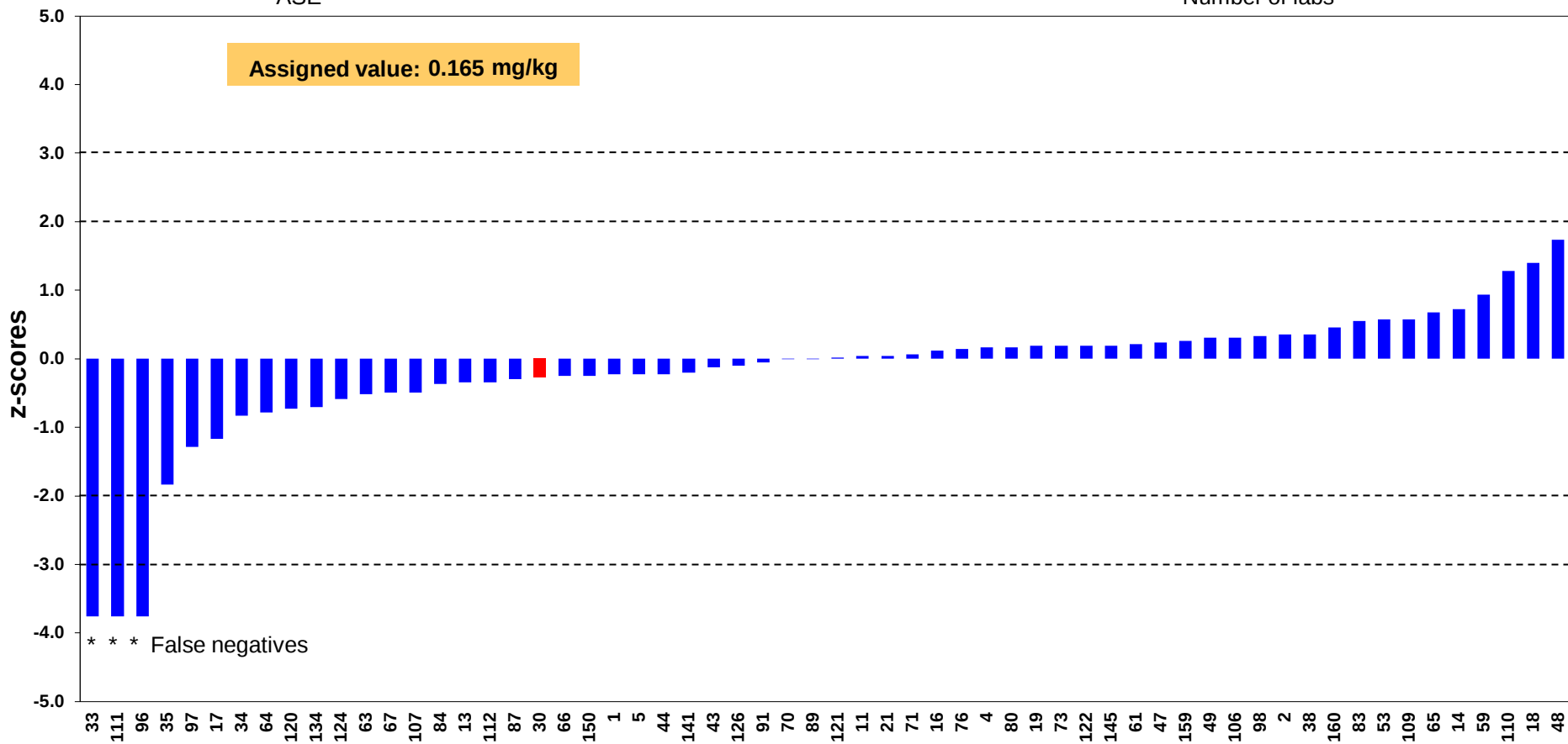


- Water added
- No water added
- Not specified
- ASE

Fluxapyroxad

Acceptable	57	(95%)
Questionable	0	(0%)
Unacceptable	3	(5%)
Number of labs	60	

Assigned value: 0.165 mg/kg

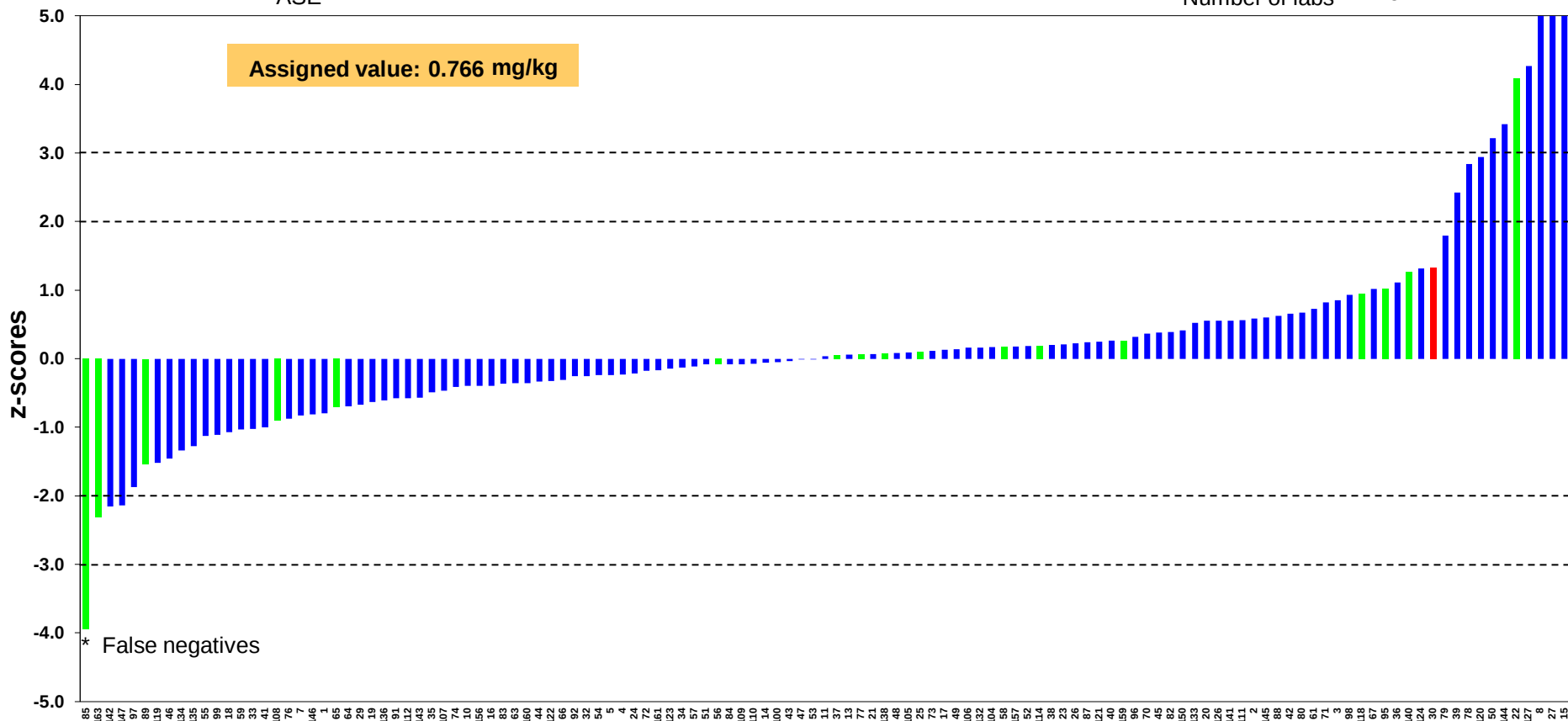


- Water added
- No water added
- Not specified
- ASE

Cypermethrin

Acceptable	106	(84%)
Questionable	11	(10%)
Unacceptable	8	(6%)
Number of labs	125	

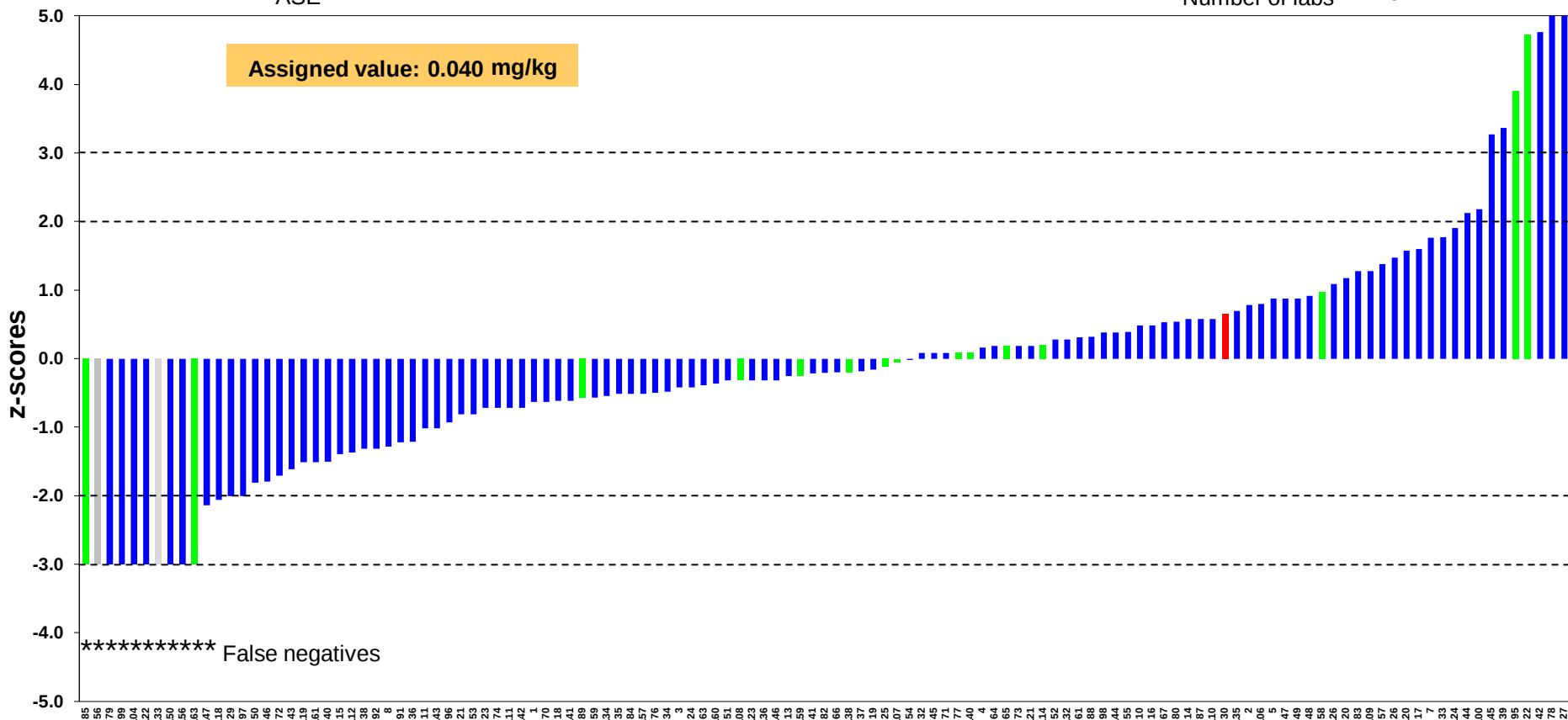
Assigned value: 0.766 mg/kg



- Water added
- No water added
- Not specified
- ASE

Deltamethrin-cis

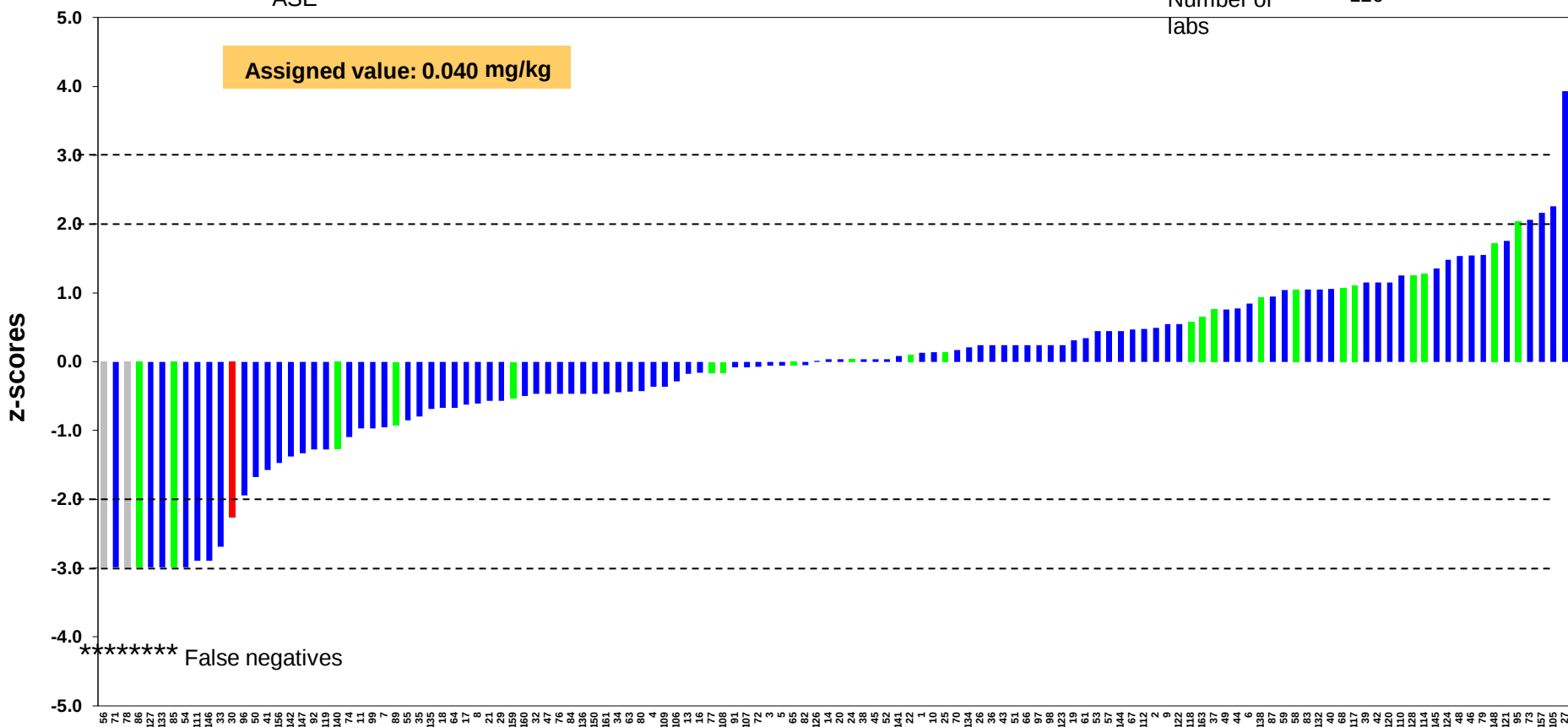
Acceptable	102	(83%)
Questionable	14	(11%)
Unacceptable	7	(6%)
Number of labs	123	



- Water added
- No water added
- Not specified
- ASE

Endosulfan-sulfate

Acceptable 110 (87%)
Questionable 15 (13%)
Unacceptable 1 (1%)
Number of labs 126

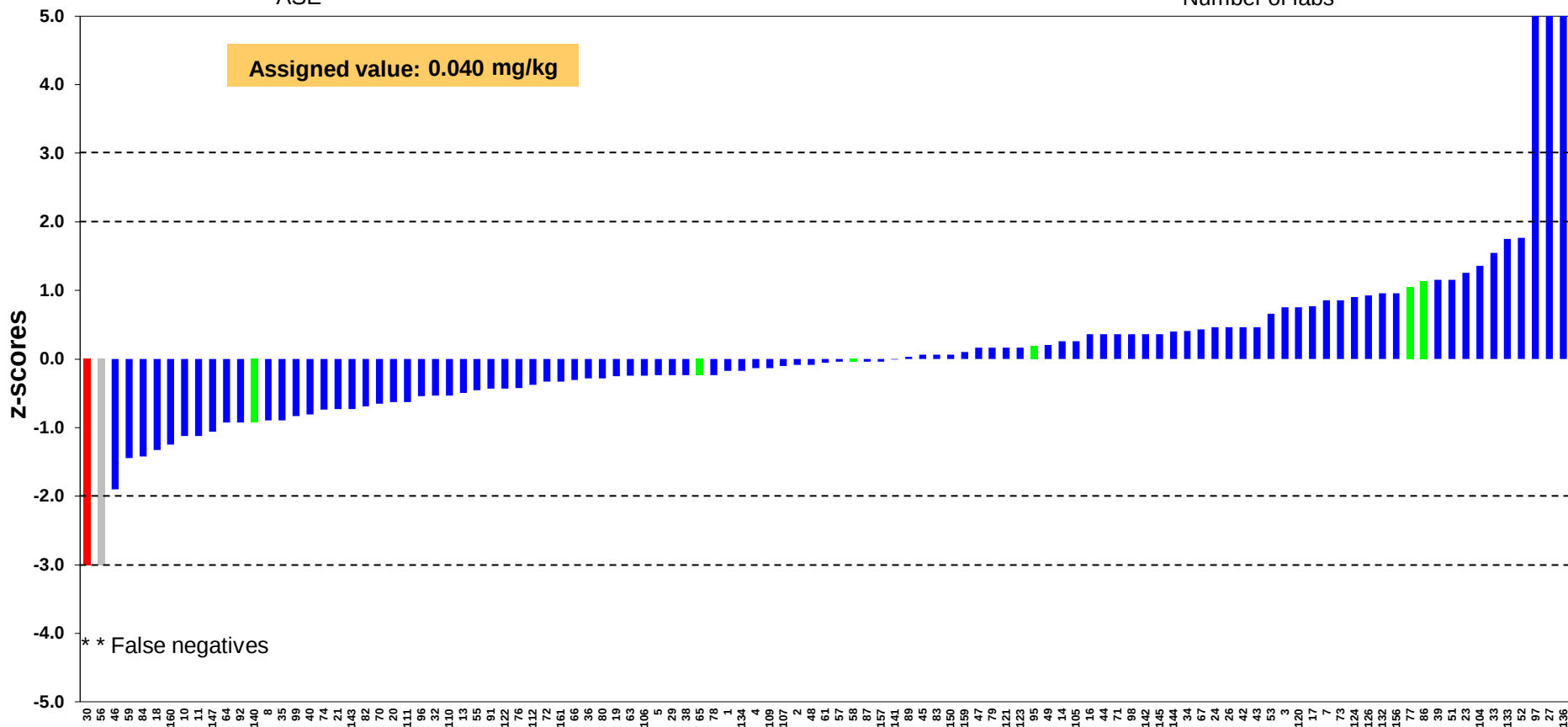


- Water added
- No water added
- Not specified
- ASE

Trifluralin

Acceptable	102	(96%)
Questionable	1	(1%)
Unacceptable	3	(3%)
Number of labs	106	

Assigned value: 0.040 mg/kg

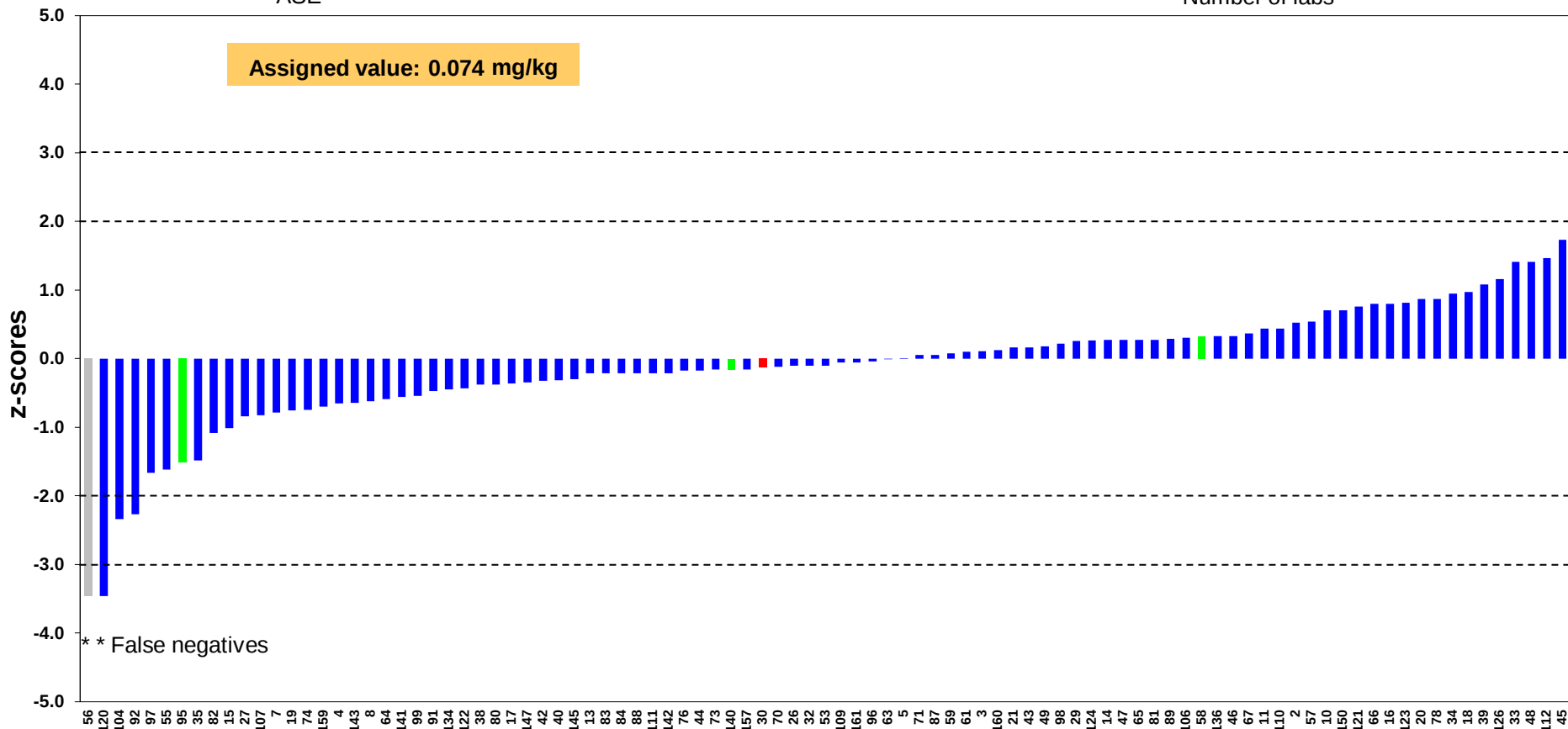


- Water added
- No water added
- Not specified
- ASE

Linuron

Acceptable	91	(97%)
Questionable	2	(1%)
Unacceptable	2	(2%)
Number of labs	95	

Assigned value: 0.074 mg/kg

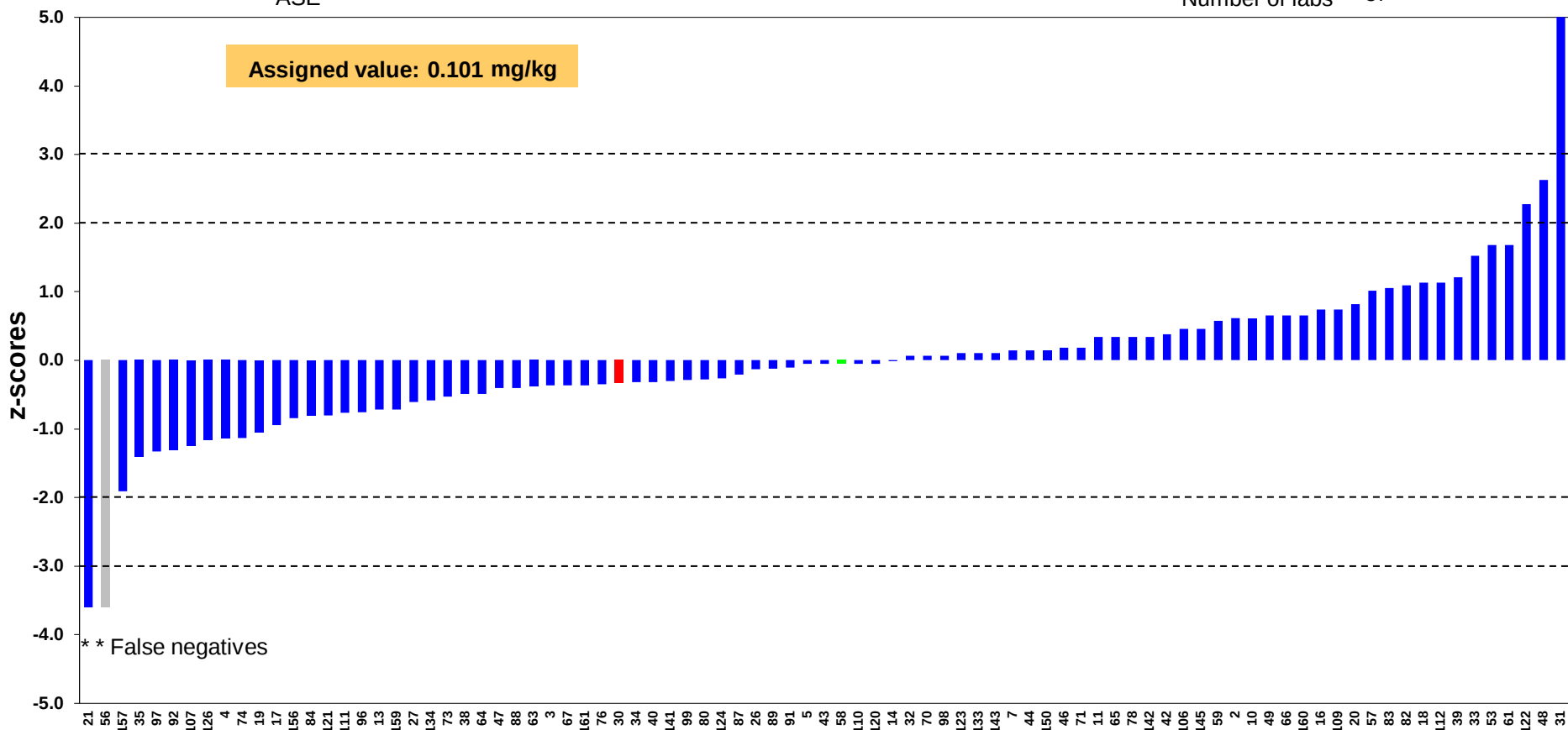


- Water added
- No water added
- Not specified
- ASE

Metconazole

Acceptable	82	(94%)
Questionable	2	(1%)
Unacceptable	3	(2%)
Number of labs	87	

Assigned value: 0.101 mg/kg

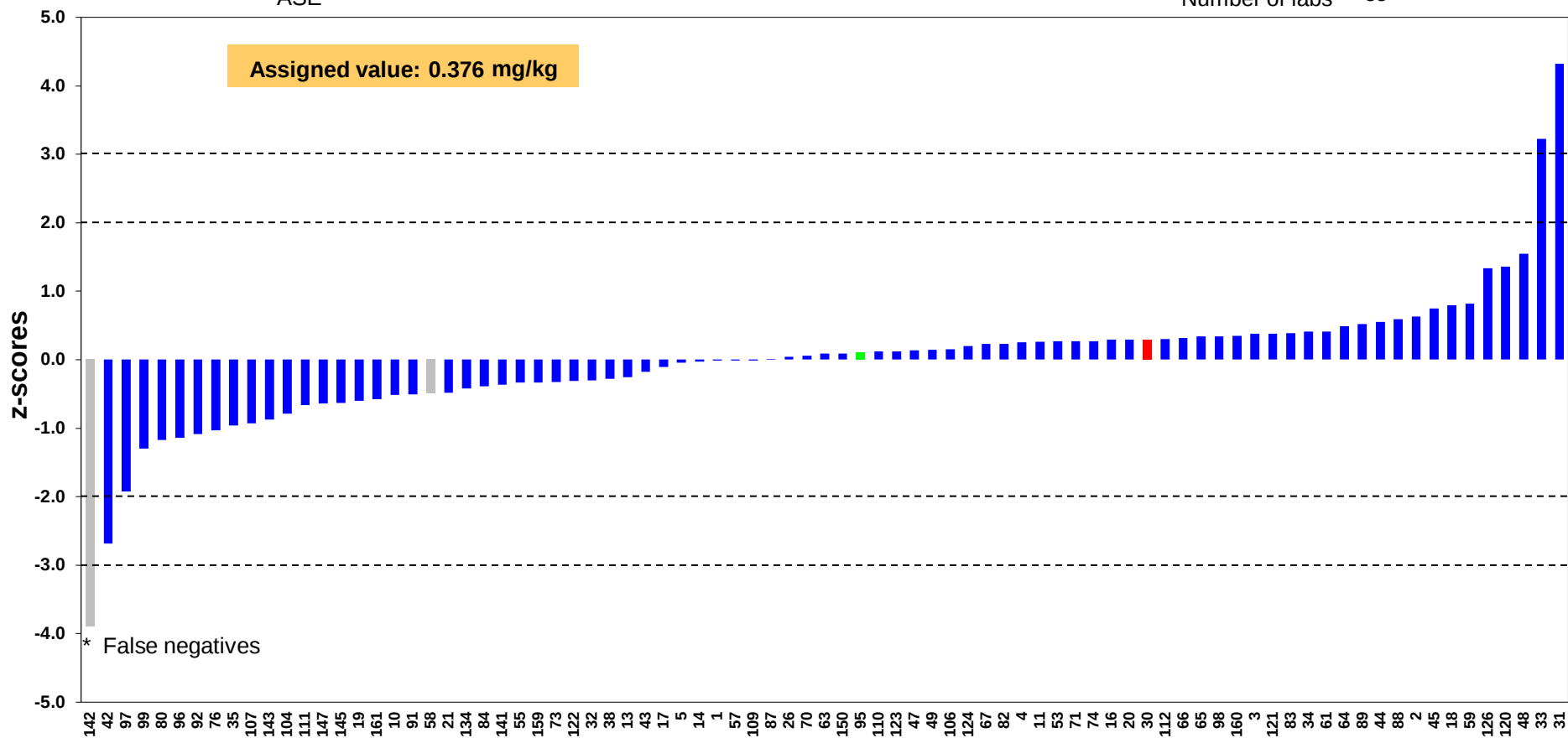


- Water added
- No water added
- Not specified
- ASE

Metrafenone

Acceptable	79	(95%)
Questionable	1	(1%)
Unacceptable	3	(4%)
Number of labs	83	

Assigned value: 0.376 mg/kg

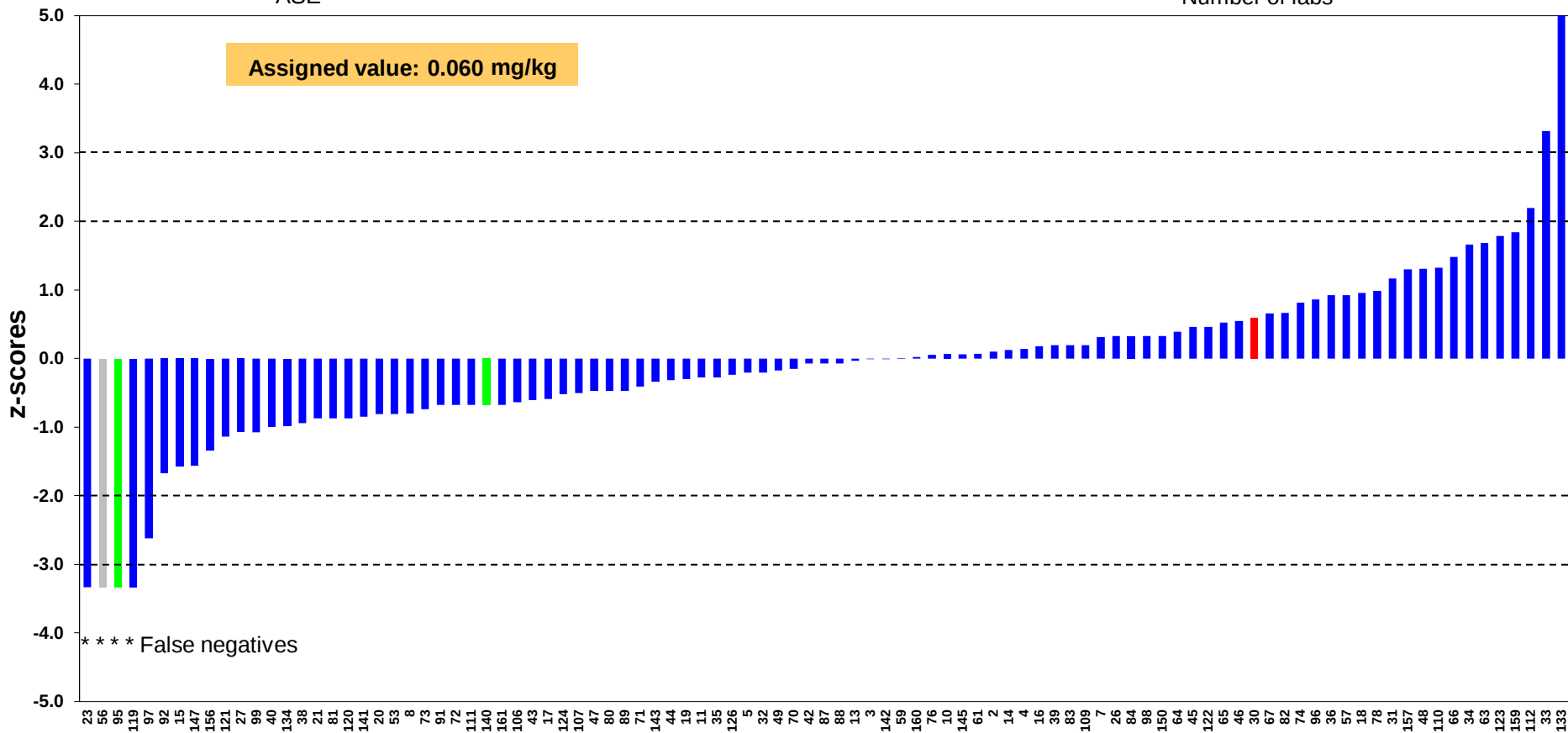


- Water added
- No water added
- Not specified
- ASE

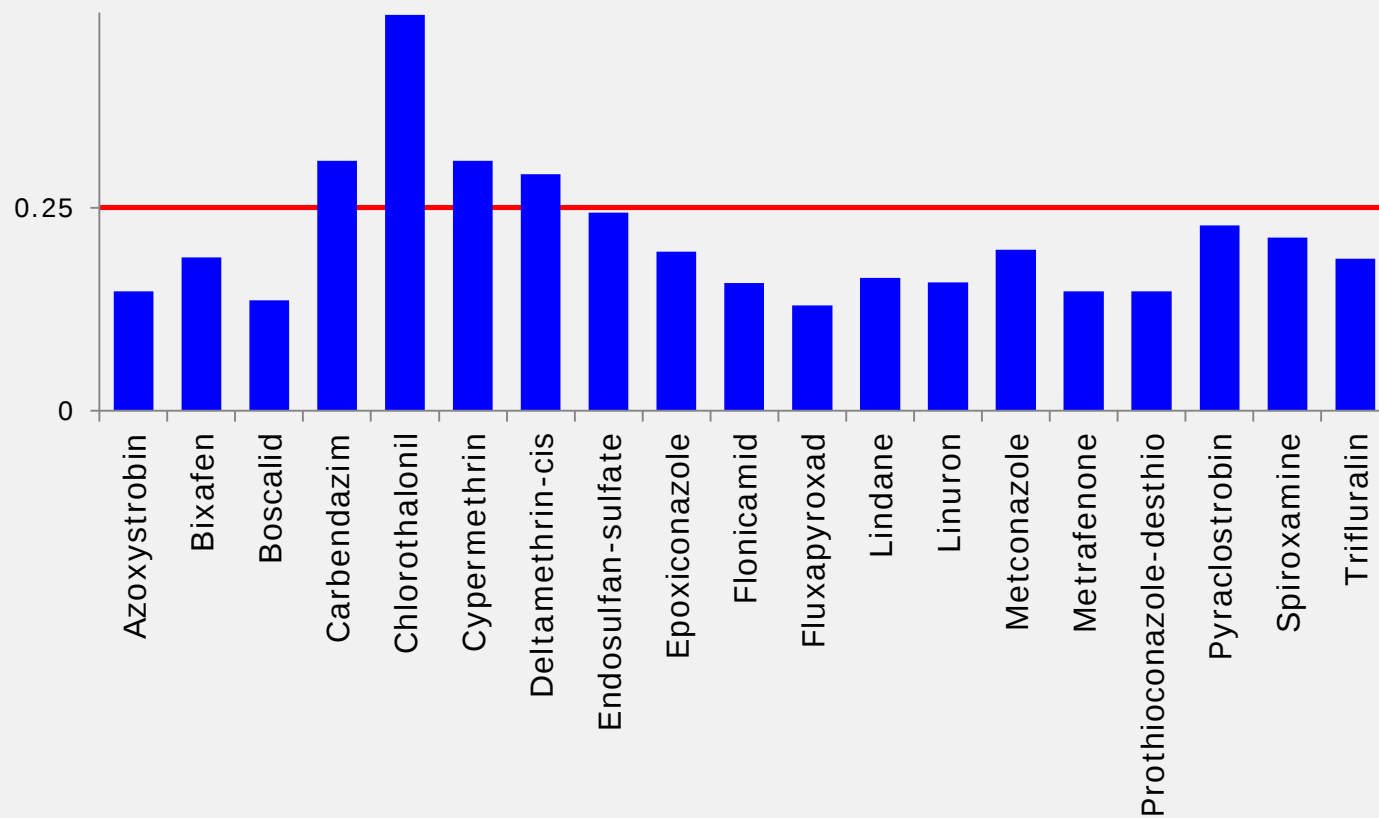
Spirooxamine

Acceptable	89	(92%)
Questionable	2	(2%)
Unacceptable	6	(6%)
Number of labs	97	

Assigned value: 0.060 mg/kg



Alg. A RSD



Acceptable, questionable and unacceptable results

	No. of reported results	Assigned values	Acceptable	Questionable	Unacceptable	False negatives
Azoxystrobin	117	0.228	114	1	2	2
Bixafen	67	0.079	65	2	0	0
Boscalid	117	0.328	112	3	2	1
Carbendazim	98	0.073	81	5	12	1
<i>Chlorothalonil</i>	91	0.042	51	31	9	23
Cypermethrin	126	0.766	106	12	8	1
Deltamethrin-cis	124	0.040	102	14	8	11
Endosulfan-sulfate	127	0.040	110	16	1	8
Epoxiconazole	110	0.117	104	3	3	1
Flonicamid	79	0.104	75	1	3	0
Fluxapyroxad	60	0.165	57	0	3	3
<i>Lindane</i>	126	0.038	112	10	4	6
Linuron	95	0.074	91	2	2	2
Metconazole	87	0.101	82	2	3	2
Metrafenone	83	0.376	79	1	3	1
Prothioconazole-desthio	86	0.201	78	4	4	3
Pyraclostrobin	97	0.074	89	4	4	2
Spiroxamine	97	0.060	89	2	6	4
Trifluralin	106	0.040	102	1	3	2

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<i>Lindane</i>	126	0.038	112	10	4	6
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Trifluralin	106	0.040	102	1	3	2

Catagory A laboratories and combined z-scores

- To be classified as Category A laboratory the labs had to report at least 90% of the pesticide present in the test material (≥ 17 pesticide residues) and 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
- $2 < z \leq 3$ Satisfactory
- $z > 3$ Unsatisfactory

AZ²

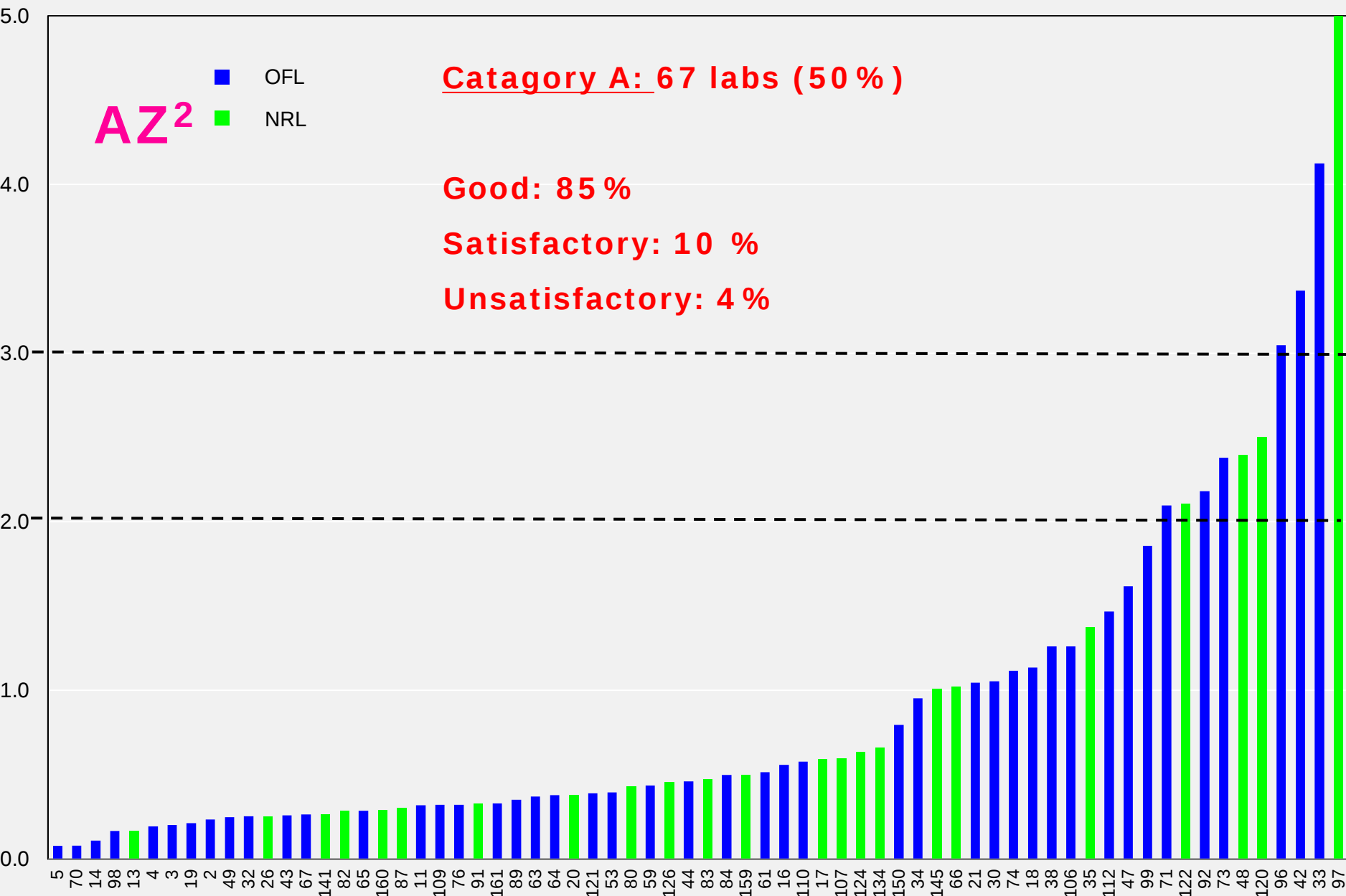
■ OFL
■ NRL

Category A: 67 labs (50 %)

Good: 85 %

Satisfactory: 10 %

Unsatisfactory: 4 %



EUPT-CF9

- Test Item
 - Maize. Kernels from a fodder variety
- Planned shipment date
 - 13 April 2015



Thank you for your attention