



EUURL

European Union Reference Laboratory for Pesticide Residues in Fruits & Vegetables

EUPT-FV-18

European Proficiency Test FV-18

EUPT-Panel

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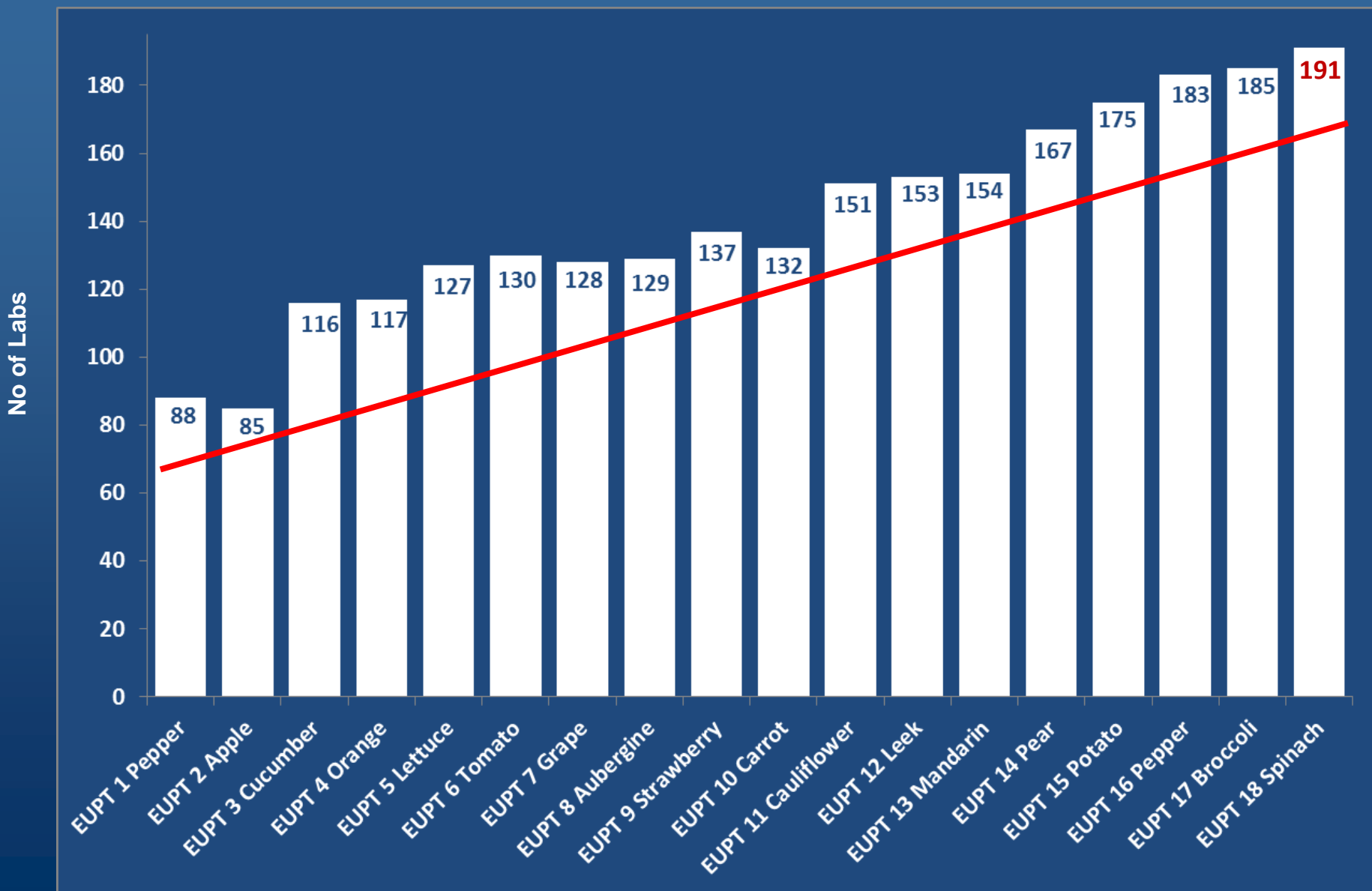
QUALITY CONTROL GROUP

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Participation



Participation

Total No. of Labs = 191

EU/EFTA Labs = 175

Other countries Labs = 16

Total No. of Countries = 43

EU/EFTA countries = 31

Other countries = 12

Participation

Member State	Laboratories
Austria	2
Belgium	7
Bulgaria	3
Croatia	7
Cyprus	2
Czech republic	3
Denmark	2
Estonia	3
Finland	2
France	8
Germany	28
Greece	9
Hungary	4
Iceland	1
Ireland	1

Member State	Laboratories
Italy	21
Latvia	1
LITHUANIA	2
Luxembourg	2
Malta	1
Norway	1
Poland	13
Portugal	2
Romania	4
Slovakia	2
Slovenia	3
Spain	32
Sweden	2
Switzerland	3
The Netherlands	1
United Kingdom	5

Other Countries	Laboratories
China	3
Colombia	1
Costa Rica	2
Egypt	1
India	1
Indonesia	1
Israel	1
Kenya	1
Panama	1
Serbia	2
Thailand	1
Turkey	1

190 pesticides

Acephate	Chlorfenapyr	Dimethoate	Fenpropathrin
Acetamiprid	Chlorfenvinphos	Dimethomorph	Fenpropidin
Acrinathrin	Chlorobenzilate	DMST	Fenpropimorph
Aldicarb	Chlorothalonil	Diniconazole	Fenpyroximate
Aldicarb Sulfone	Chlorpropham	Diphenylamine	Fenthion
Aldicarb Sulfoxide	Chlorpyrifos	Endosulfan alpha	Fenthion oxon
Aldrin	Chlorpyrifos-methyl	Endosulfan beta	Fenthion oxon sulfone
Azinphos-methyl	Clofentezine	Endosulfan sulfate	Fenthion oxon sulfoxide
Azoxystrobin	Clothianidin	EPN	Fenthion sulfone
Benfuracarb	Cyfluthrin	Epoxiconazole	Fenthion sulfoxide
Bifenthrin	Cymoxanil	Ethion	Fenvalerate/Esfenvalerate
Biphenyl	Cypermethrin	Ethirimol	Fipronil
Bitertanol	Cyproconazole	Ethoprophos	Fludioxonil
Boscalid	Cyprodinil	Etofenprox	Flufenoxuron
Bromopropylate	Deltamethrin	Famoxadone	Fluopicolide
Bromuconazole	Demeton-S-methylsulfone	Fenamidone	Fluopyram
Bupirimate	Diazinon	Fenamiphos	Fluquinconazole
Buprofezin	Dichlofluanid	Fenamiphos sulfone	Flusilazole
Cadusafos	Dichlorvos	Fenamiphos sulfoxide	Flutolanil
Carbaryl	Dicloran	Fenarimol	Flutriafol
Carbendazim and benomyl	Dicofol	Fenazaquin	Fosthiazate
Carbofuran	Dieldrin	Fenbuconazole	Hexaconazole
Carbofuran-3-hydroxy	Diethofencarb	Fenhexamid	Hexythiazox
Carbosulfan	Difenoconazole	Fenitrothion	Imazalil
Chlorantraniliprole	Diflubenzuron	Fenoxycarb	Imidacloprid

8 New compounds



Indoxacarb
 Iprodione
 Iprovalicarb
 Isocarbophos
 Isofenphos-methyl
 Isoprothiolane
 Kresoxim-methyl
 Lambda-Cyhalothrin
 Linuron
 Lufenuron
 Malaoxon
 Malathion
 Mandipropamid
 Mepanipyrim
 Metaflumizone
 Metalaxyl and metalaxyl-M
 Metconazole
 Methamidophos
 Methidathion
 Methiocarb
 Methiocarb sulfone
 Methiocarb sulfoxide
 Methomyl
 Methoxyfenozide
 Monocrotophos

Myclobutanyl
 Omethoate
 Orthophenylphenol
 Oxadixyl
 Oxamyl
 Oxydemeton-methyl
 Paclobutrazole
 Paraoxon-methyl
 Parathion-ethyl
 Parathion-methyl
 Penconazole
 Pencycuron
 Pendimethalin
 Permethrin
 Phenthoate
 Phosalone
 Phosmet
 Phosmet oxon
 Phoxim
 Pirimicarb
 Pirimicarb-desmethyl
 Pirimiphos-methyl
 Prochloraz
 Procymidone
 Profenofos

Propamocarb
 Propargite
 Propiconazole
 Propyzamide
 Prothioconazole
 Prothiofos
 Pyraclostrobin
 Pyridaben
 Pyrimethanil
 Pyriproxyfen
 Quinoxifen
 Spinosad
 Spirodiclofen
 Spiroxamine
 Tau-Fluvalinate
 Tebuconazole
 Tebufenozide
 Tebufenpyrad
 Teflubenzuron
 Tefluthrin
 Terbutylazine
 Tetraconazole
 Tetradifon
 Thiabendazole
 Thiacloprid

Thiamethoxam
 Thiodicarb
 Thiophanate-methyl
 Tolclofos-methyl
 Tolyfluanid
 Triadimefon
 Triadimenol
 Triazophos
 Trichlorfon
 Trifloxystrobin
 Triflumuron
 Trifluralin
 Trificonazole
 Vinclozolin
 Zoxamide

Spiromesifen

8 New compounds

25 pesticides

Working Document SANTE/12745/2013

(Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin)

- Ametoctradin
- Benalaxyl including other mixtures of constituent isomers including benalaxyl-M (sum of isomers)
- Benzovindiflupyr
- Clomazone
- Cyazofamid
- Emamectin benzoate B1a, expressed as emamectin
- Etoxazole
- Fenpyrazamine
- Fluxapyroxad
- Heptachlor
- Heptachlor epoxide
- Isopyrazam
- Penflufen
- Penthiopyrad
- Prosulfocarb
- Pyrethrins
- Quintozene
- Pentachloro-aniline
- Rotenone
- Spirotetramat
- Spirotetramat metabolite BYI08330-enol
- Spirotetramat metabolite BYI08330-ketohydroxy
- Spirotetramat metabolite BYI08330-monohydroxy
- Spirotetramat metabolite BYI08330 enol-glucoside
- Tetramethrin

Pesticides used for the treatment

Chlorantraniliprole*	Fluopyram
Cymoxanil*	Imidacloprid
Cyazofamid**	Indoxacarb
Difenoconazole	Metalaxyl and Metalaxyl-M
Diflubenzuron	Omethoate***
Dimethoate	Penconazole
Famoxadone*	Thiacloprid
Fenpyrazamine**	Triadimenol
Total: 16	

*** New in the target list** ***** Not spiked**

**** Voluntary pesticides**

Calendar

ACTIVITY	DATE
- Publishing the Target Pesticide List, Calendar and Matrix on the Web page.	9 th November 2015
- Receiving Application Form from invited laboratories.	1 st Dec-11 th Jan 2016
- Specific Protocol published on the Web site.	25 th January 2016 at the latest
- Deadline for receiving Laboratory scope: Form 0	25 th Jan-5 th Feb 2016
- Sample distribution.	8 th February 2016
- Deadline for receiving sample acceptance: Form 1	12 th February 2016
- Deadline for receiving results: Forms 2, 3 and 4	1 st March 2016
- Filling in Form 5	7 th -11 th March 2016
- Preliminary Report: only results, no statistical treatment.	Last week of March 2016
- Final Report distributed to the Laboratories.	December 2016

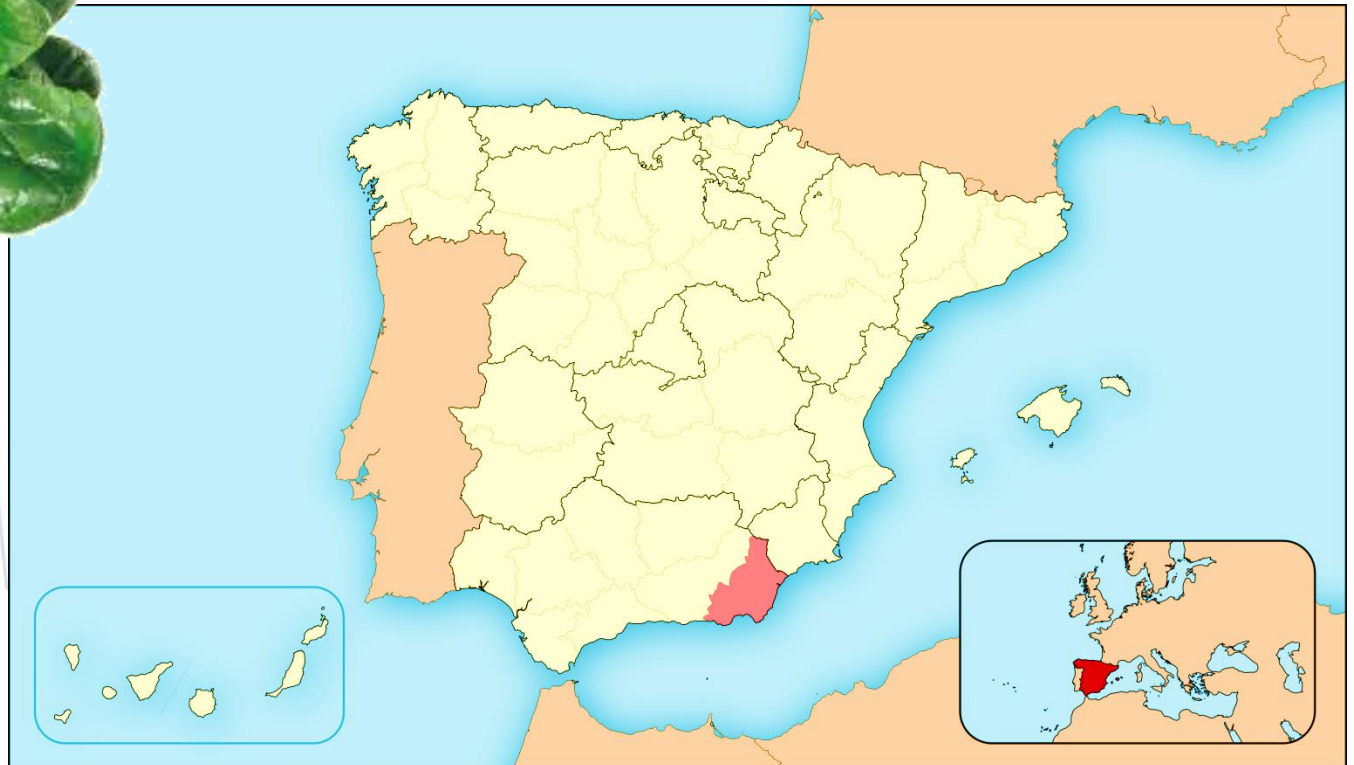
EUPT-FV-18

European Proficiency Test FV-18

Spinach



Organic spinachs were grown in a greenhouse in Almería, Spain.





Before harvest, the spinachs were treated with commercial formulations



Preparation of the test item



Homogeneity

The homogeneity in the treated sample was studied using the 2006 Harmonised Protocol.

Stability

1st Analysis - prior to the sample shipment

2nd Analysis - after the deadline for reporting results

3rd Analysis - reproducing the delivery conditions that the samples experienced during 48 hours

All the pesticides passed the homogeneity test

All the pesticides passed the stability test

Results

Assigned values

Mandatory Pesticides

	Robust Mean X* (mg/kg)
Chlorantraniliprole	3.071
Cymoxanil	0.011 ⁺
Difenoconazole	0.837
Diflubenzuron	1.121
Dimethoate	0.036
Famoxadone	1.026
Fluopyram	0.289
Imidacloprid	0.250
Indoxacarb (sum of indoxacarb and its R enantiomer)	1.436
Metalaxyl and metalaxyl-M	0.058
Omethoate	0.142
Penconazole	0.016 ⁺
Thiacloprid	0.516
Triadimenol	0.205

Voluntary Pesticides

	Robust Mean X* (mg/kg)
Cyazofamid	0.279
Fenpyrazamine	0.357

Assigned values

Voluntary Pesticides

0.011-0.100 mg/kg

	Robust Mean X* (mg/kg)
Cymoxanil	0,011
Penconazole	0,016
Dimethoate	0,036
Metalaxyl and metalaxyl-M	0,058
Omethoate	0,142
Triadimenol	0,205
Imidacloprid	0,250
Cyazofamid	0,279
Fluopyram	0,289
Fenpyrazamine	0,357
Thiacloprid	0,516
Difenoconazole	0,837
Famoxadone	1,026
Diflubenzuron	1,121
Indoxacarb (sum of indoxacarb and its R enantiomer)	1,436
Chlorantraniliprole	3,071

Assigned values

Voluntary Pesticides

0.011-0.100 mg/kg

0.100-0.500 mg/kg

	Robust Mean X* (mg/kg)
Cymoxanil	0,011
Penconazole	0,016
Dimethoate	0,036
Metalaxyl and metalaxyl-M	0,058
Omethoate	0,142
Triadimenol	0,205
Imidacloprid	0,250
Cyazofamid	0,279
Fluopyram	0,289
Fenpyrazamine	0,357
Thiacloprid	0,516
Difenoconazole	0,837
Famoxadone	1,026
Diflubenzuron	1,121
Indoxacarb (sum of indoxacarb and its R enantiomer)	1,436
Chlorantraniliprole	3,071

Assigned values

Voluntary Pesticides

0.011-0.100 mg/kg

0.100-0.500 mg/kg

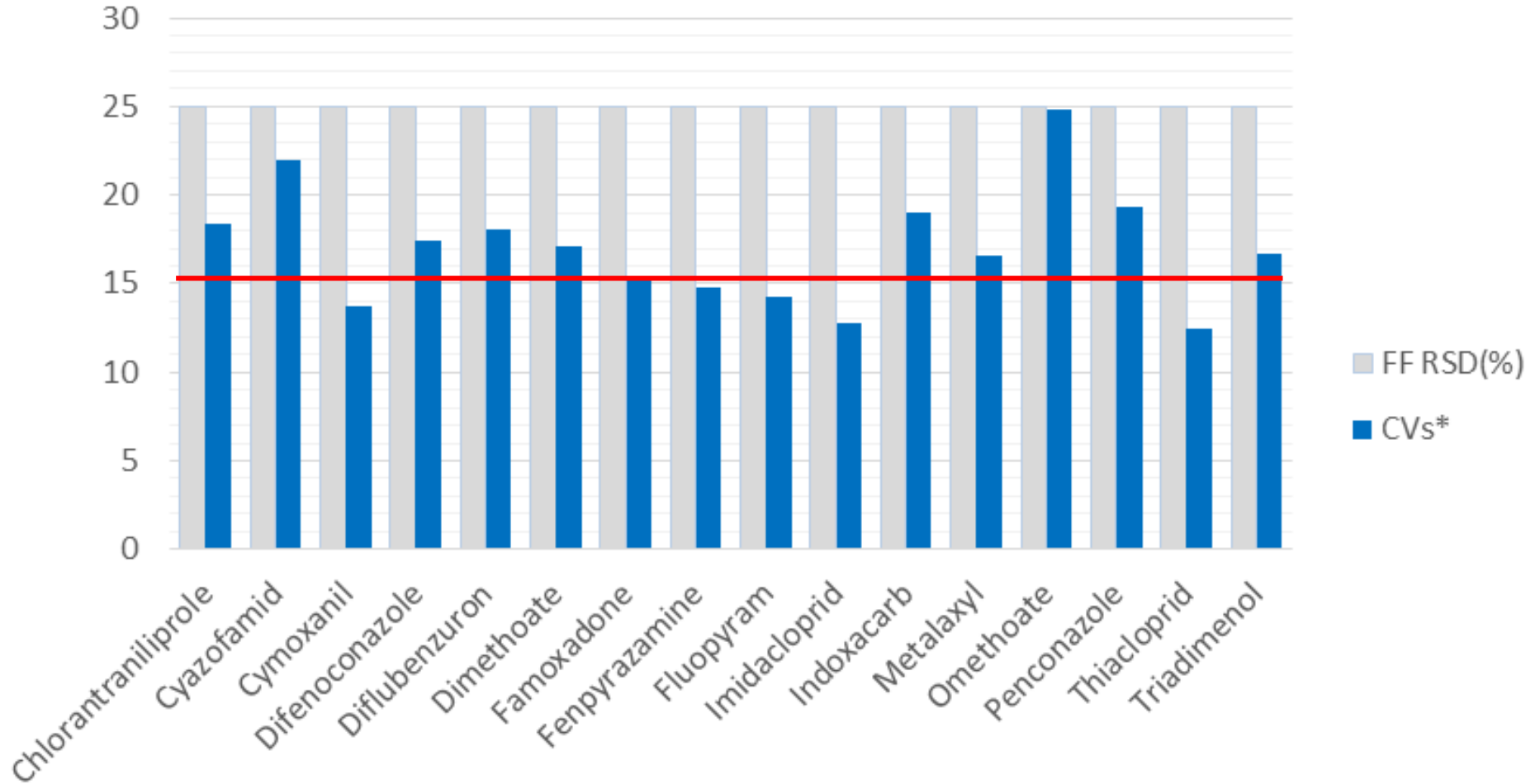
> 0.500 mg/kg

	Robust Mean X* (mg/kg)
Cymoxanil	0,011
Penconazole	0,016
Dimethoate	0,036
Metalaxyl and metalaxyl-M	0,058
Omethoate	0,142
Triadimenol	0,205
Imidacloprid	0,250
Cyazofamid	0,279
Fluopyram	0,289
Fenpyrazamine	0,357
Thiacloprid	0,516
Difenoconazole	0,837
Famoxadone	1,026
Diflubenzuron	1,121
Indoxacarb (sum of indoxacarb and its R enantiomer)	1,436
Chlorantraniliprole	3,071

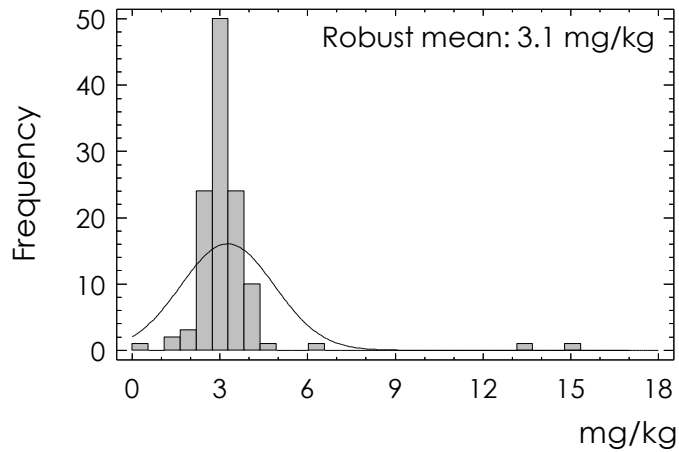


	MRRL (mg/kg)	Robust Mean X* (mg/kg)	CVs*(%)	Uncertainty	EURL-FV Analysed by
Chlorantraniliprole	0.01	3.071	18.4	0.065	LC-MS/MS
Cyazofamid	0.01	0.279	22.0	0.008	LC-MS/MS
Difenoconazole	0.01	0.837	17.5	0.015	LC-MS/MS
Diflubenzuron	0.01	1.121	18.1	0.023	LC-MS/MS
Dimethoate	0.003	0.036	17.1	0.001	LC-MS/MS
Famoxadone	0.01	1.026	15.3	0.018	LC-MS/MS
Fenpyrazamine	0.01	0.357	14.8	0.011	LC-MS/MS
Fluopyram	0.01	0.289	14.2	0.005	GC-MS/MS
Imidacloprid	0.01	0.250	12.8	0.003	LC-MS/MS
Indoxacarb (sum of indoxacarb and its R enantiomer)	0.01	1.436	19.1	0.028	LC-MS/MS
Metalaxyl and metalaxyl-M	0.01	0.058	16.5	0.001	GC-MS/MS
Omethoate	0.003	0.142	24.9	0.04	LC-MS/MS
Thiacloprid	0.01	0.516	12.5	0.007	LC-MS/MS
Triadimenol	0.01	0.205	16.6	0.003	LC-MS/MS

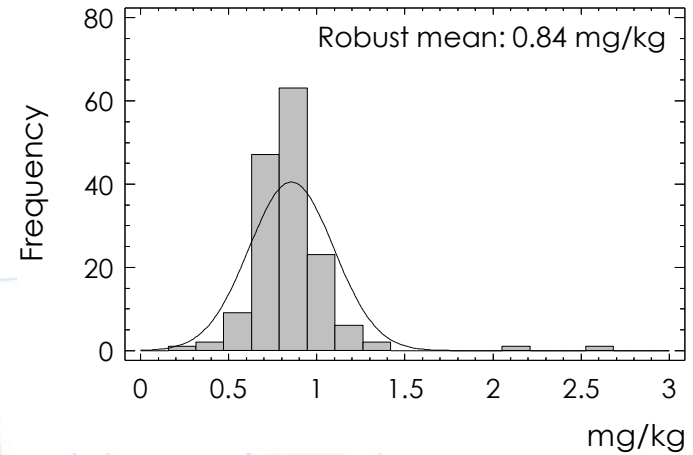
Dispersion of Results



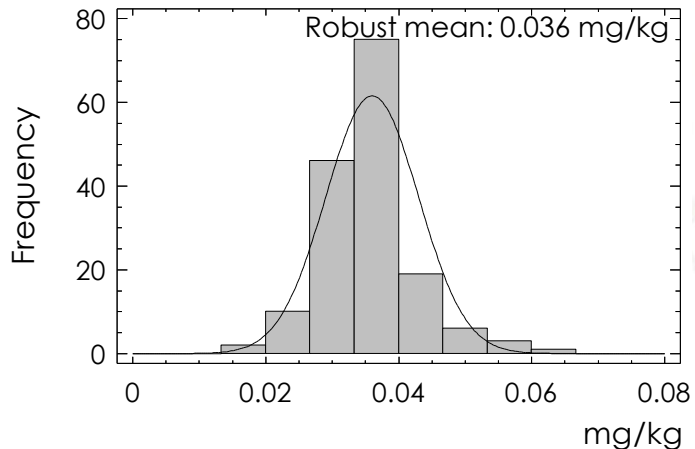
Chlorantranilprole



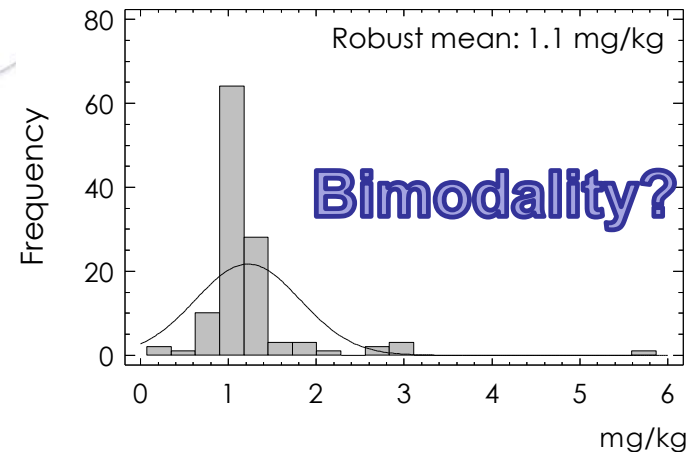
Difenoconazole



Dimethoate

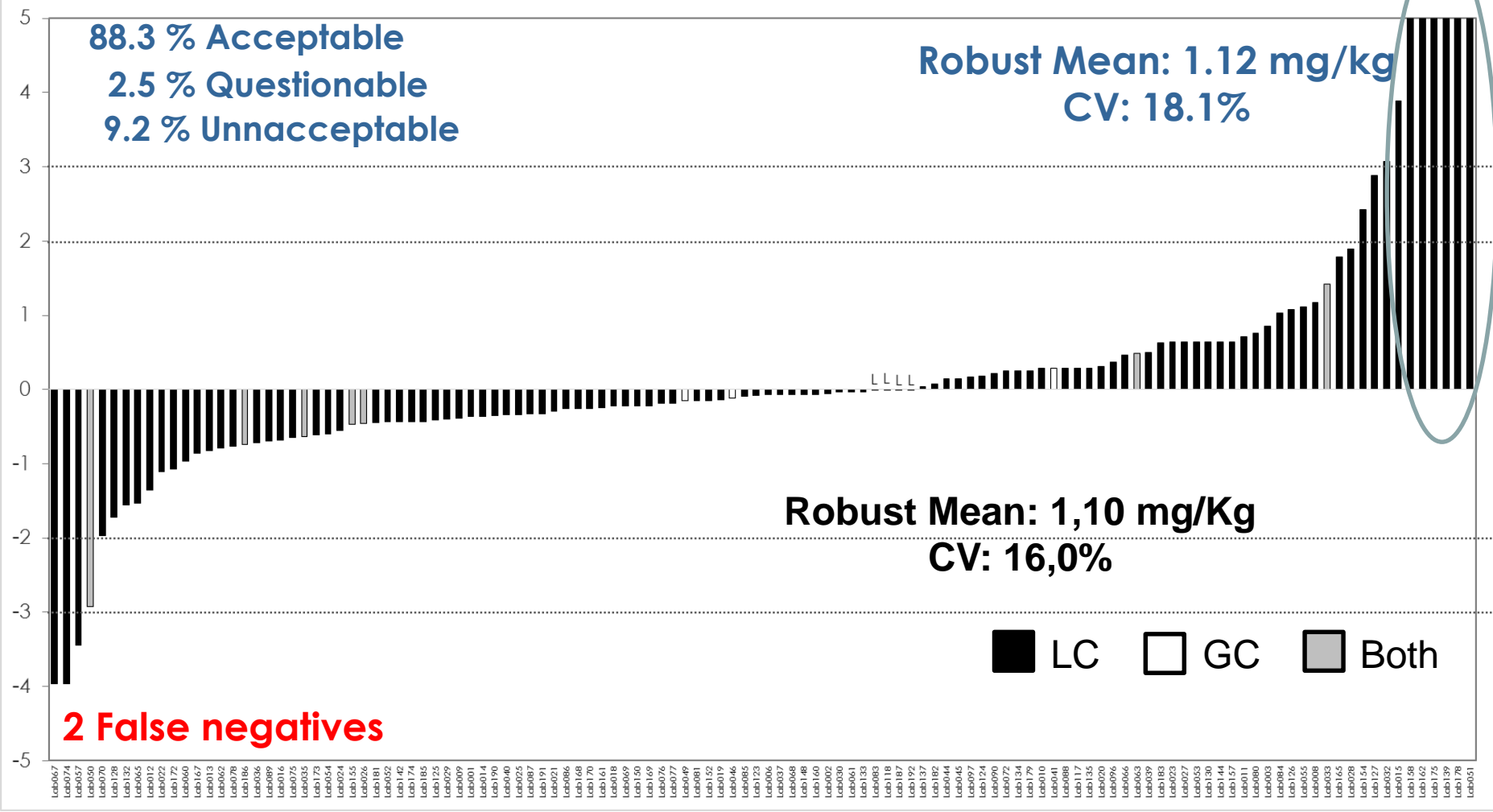


Diflubenzuron



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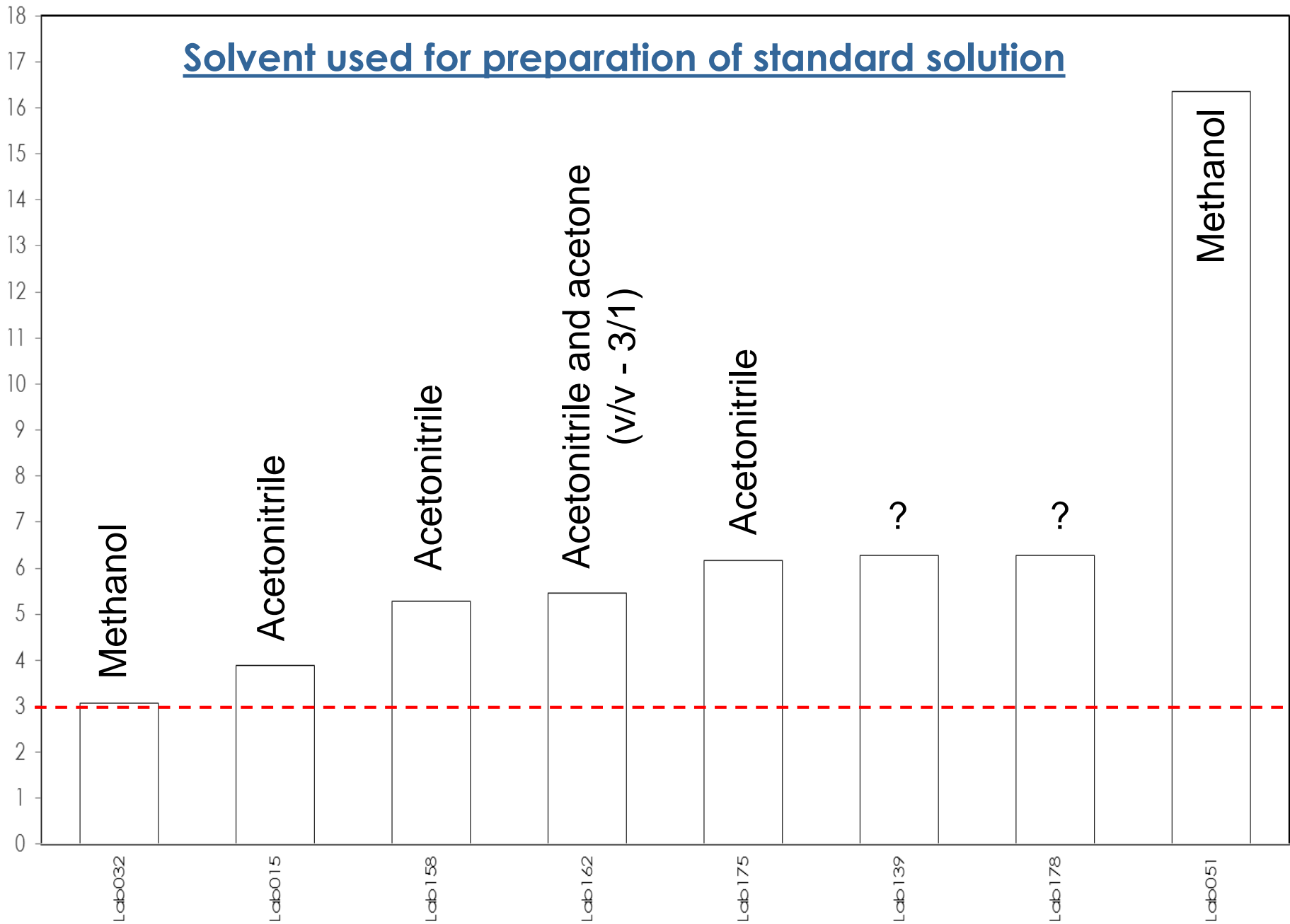
Diflubenzuron



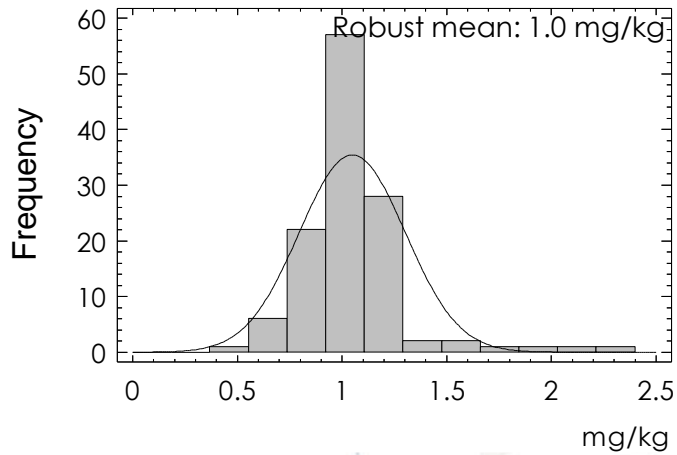
Diflubenzuron

Solvent used for preparation of standard solution

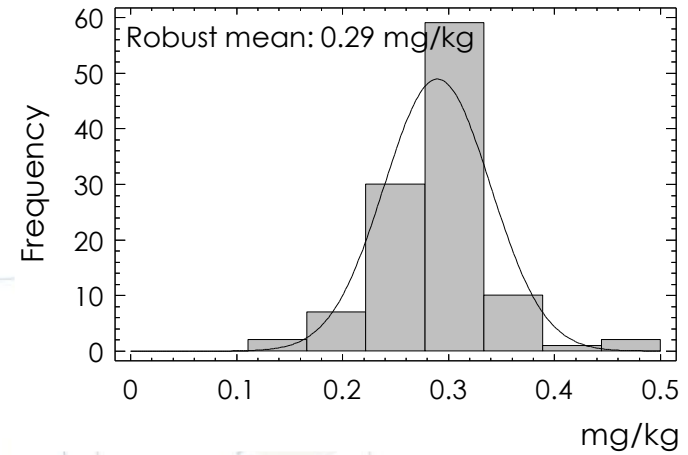
Z score



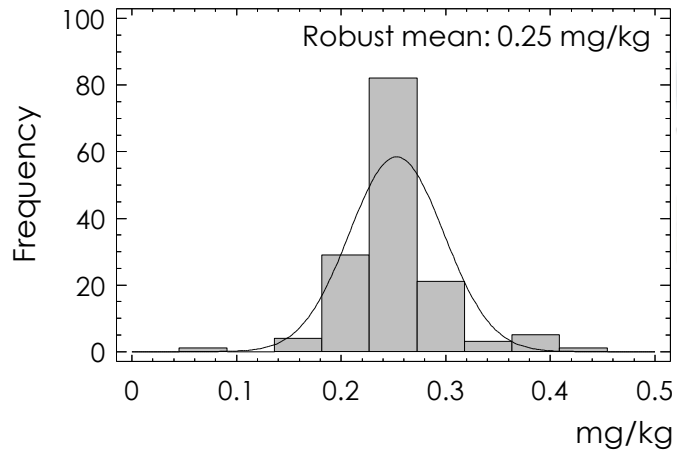
Famoxadone



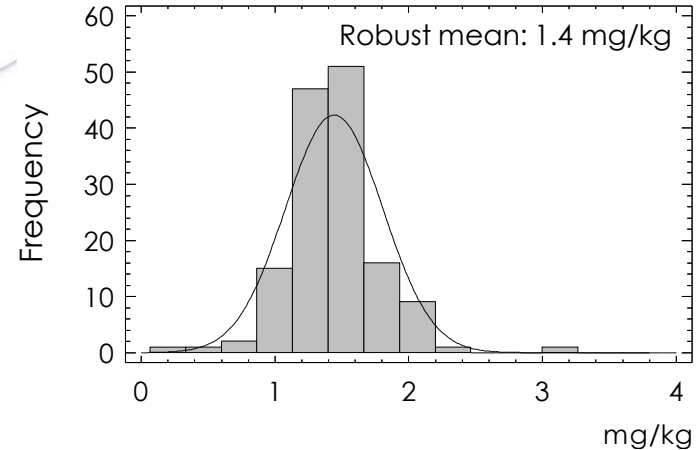
Fluopyram



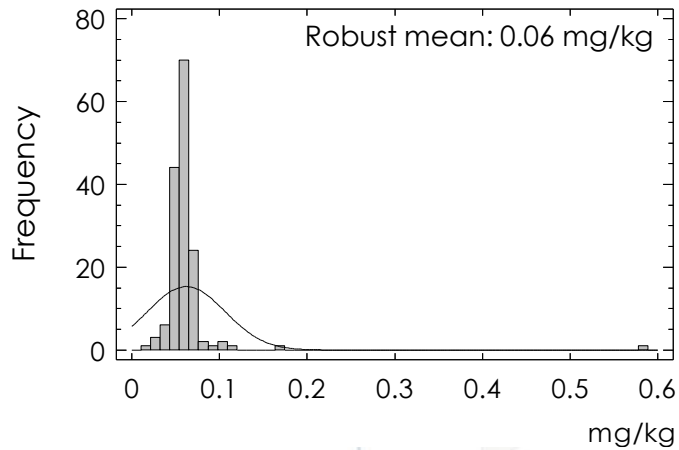
Imidacloprid



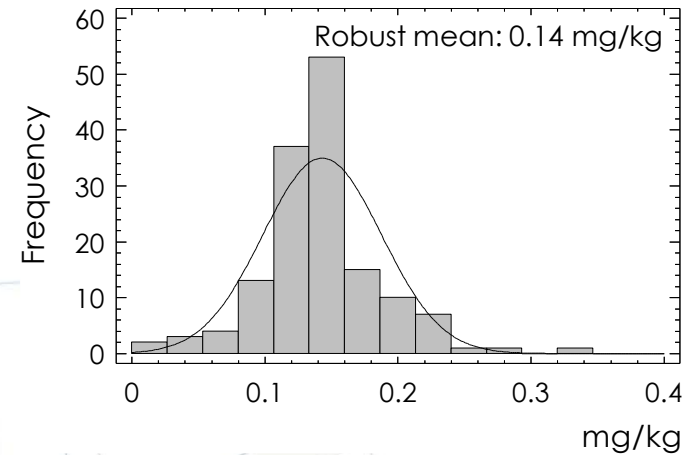
Indoxacarb



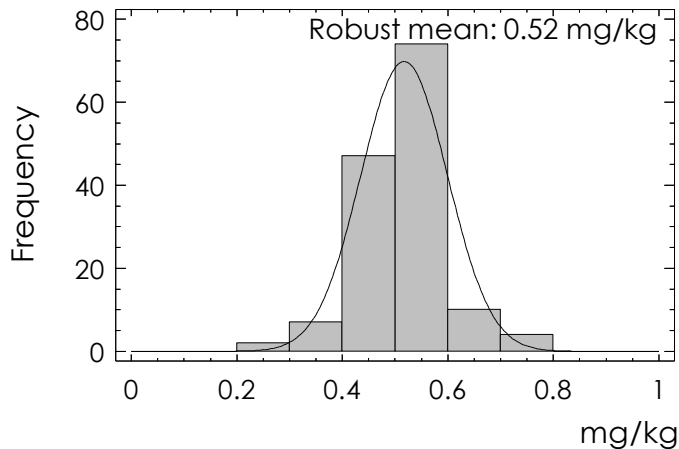
Metalaxyl and metalaxyl-M



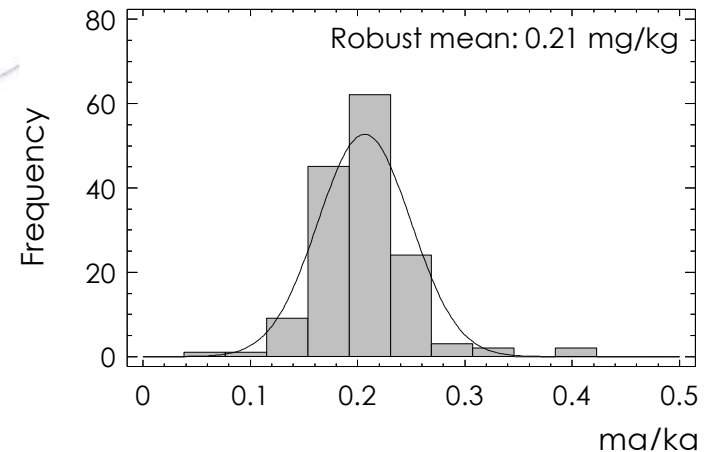
Omethoate



Thiacloprid

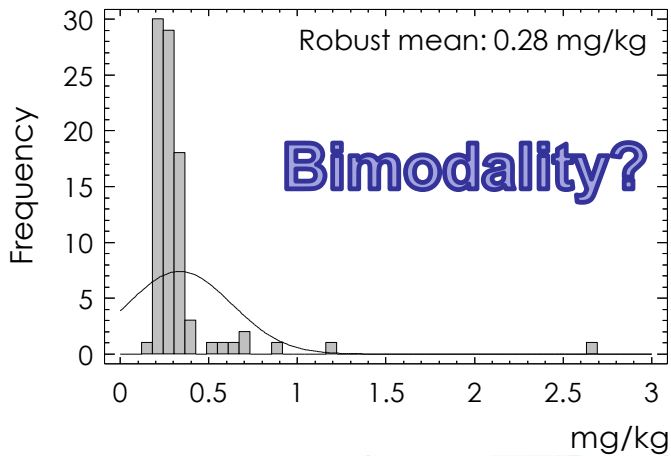


Triadimenol

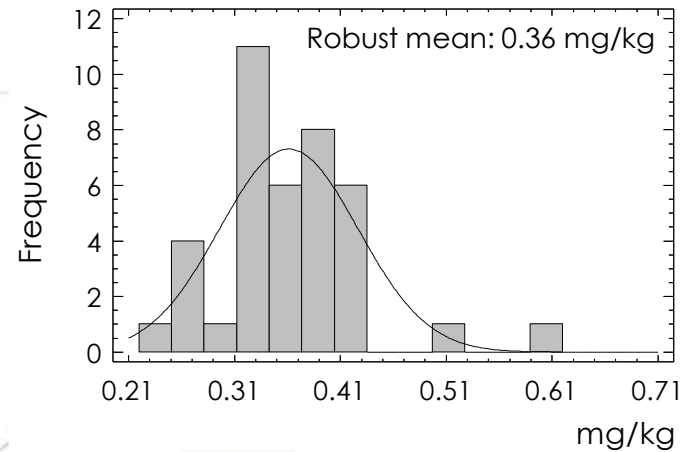


Voluntary compounds

Cyazofamid



Fenpyrazamine

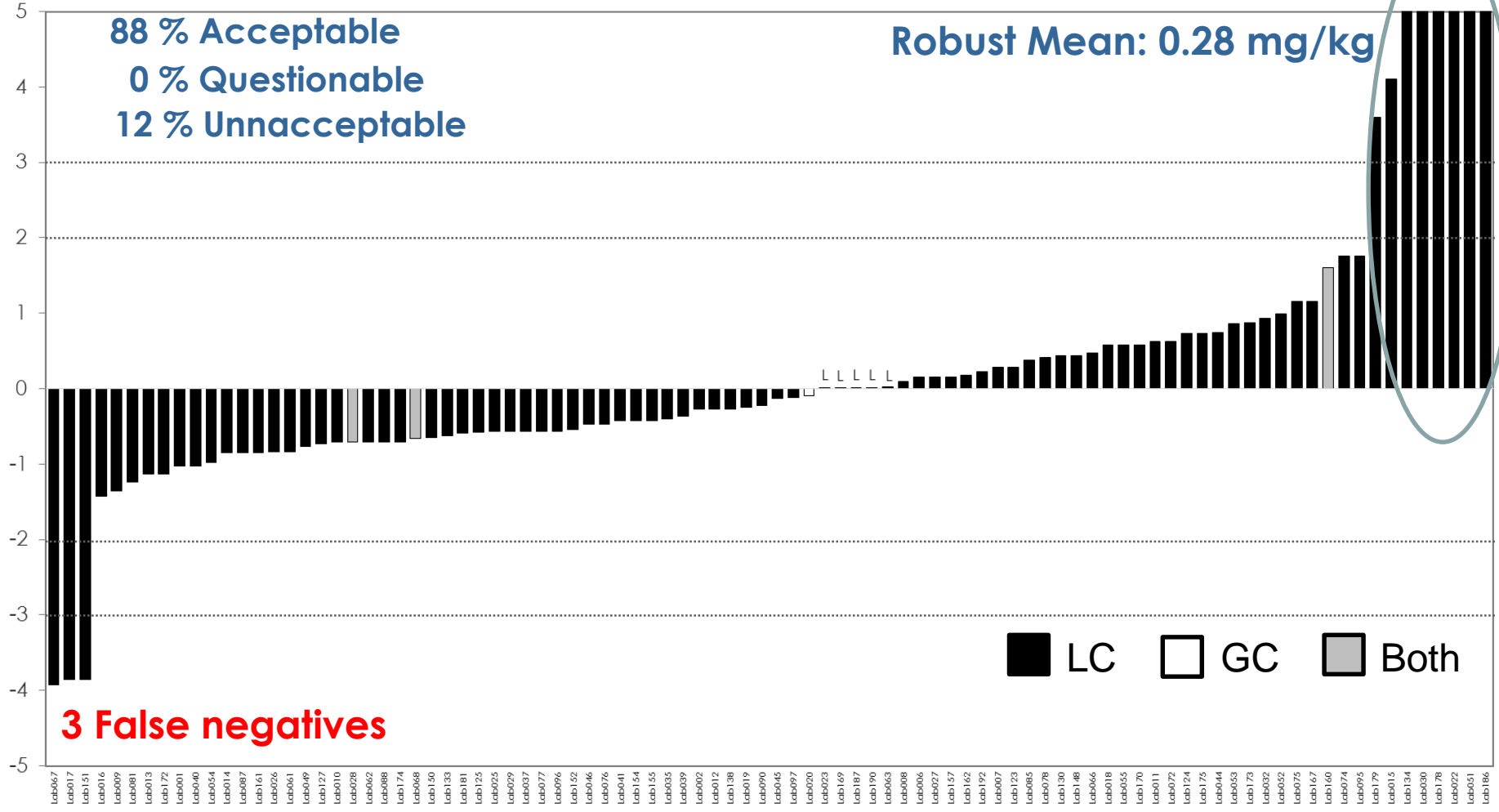


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Cyazofamid

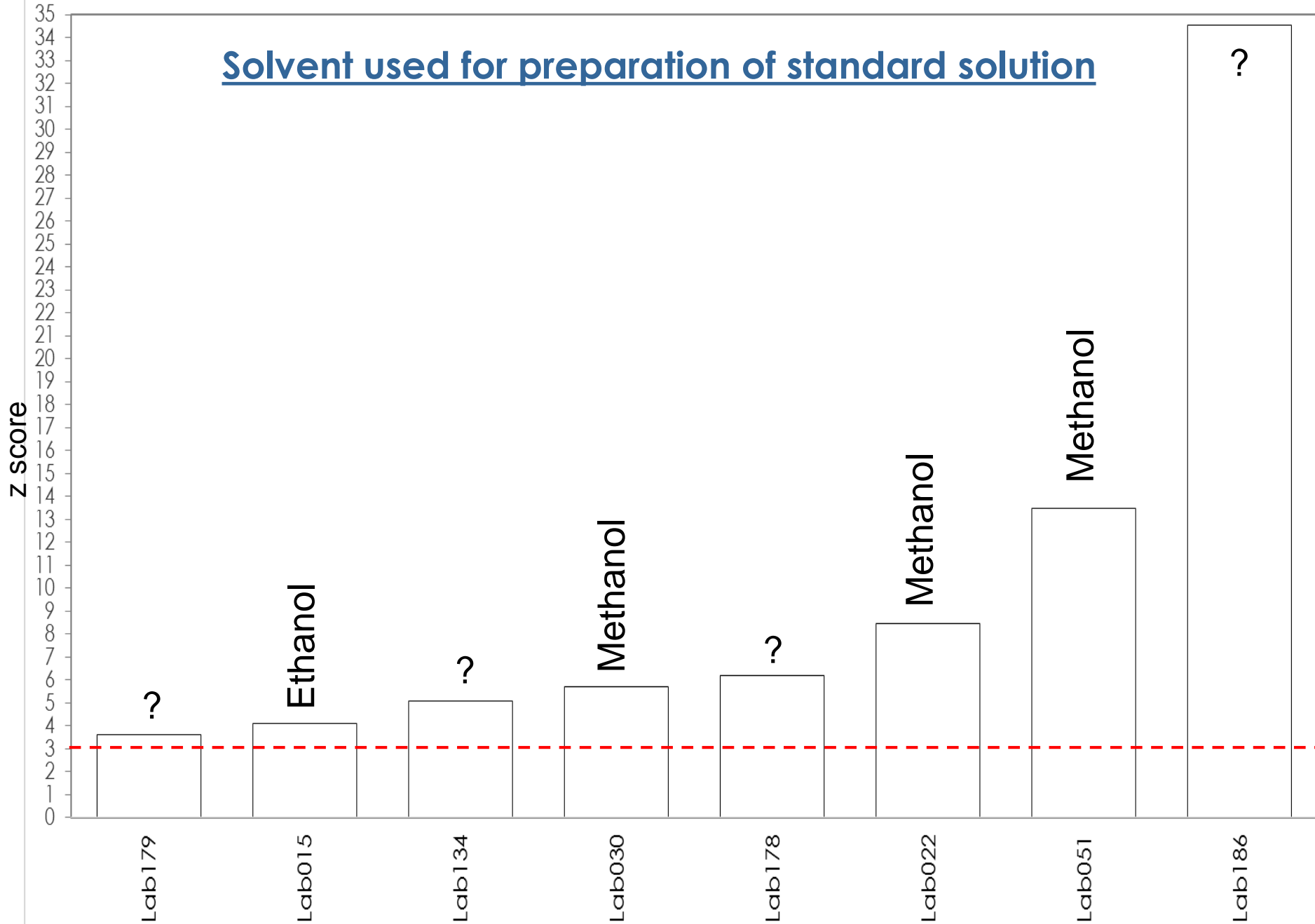
88 % Acceptable
0 % Questionable
12 % Unacceptable

Robust Mean: 0.28 mg/kg



Cyazofamid

Solvent used for preparation of standard solution

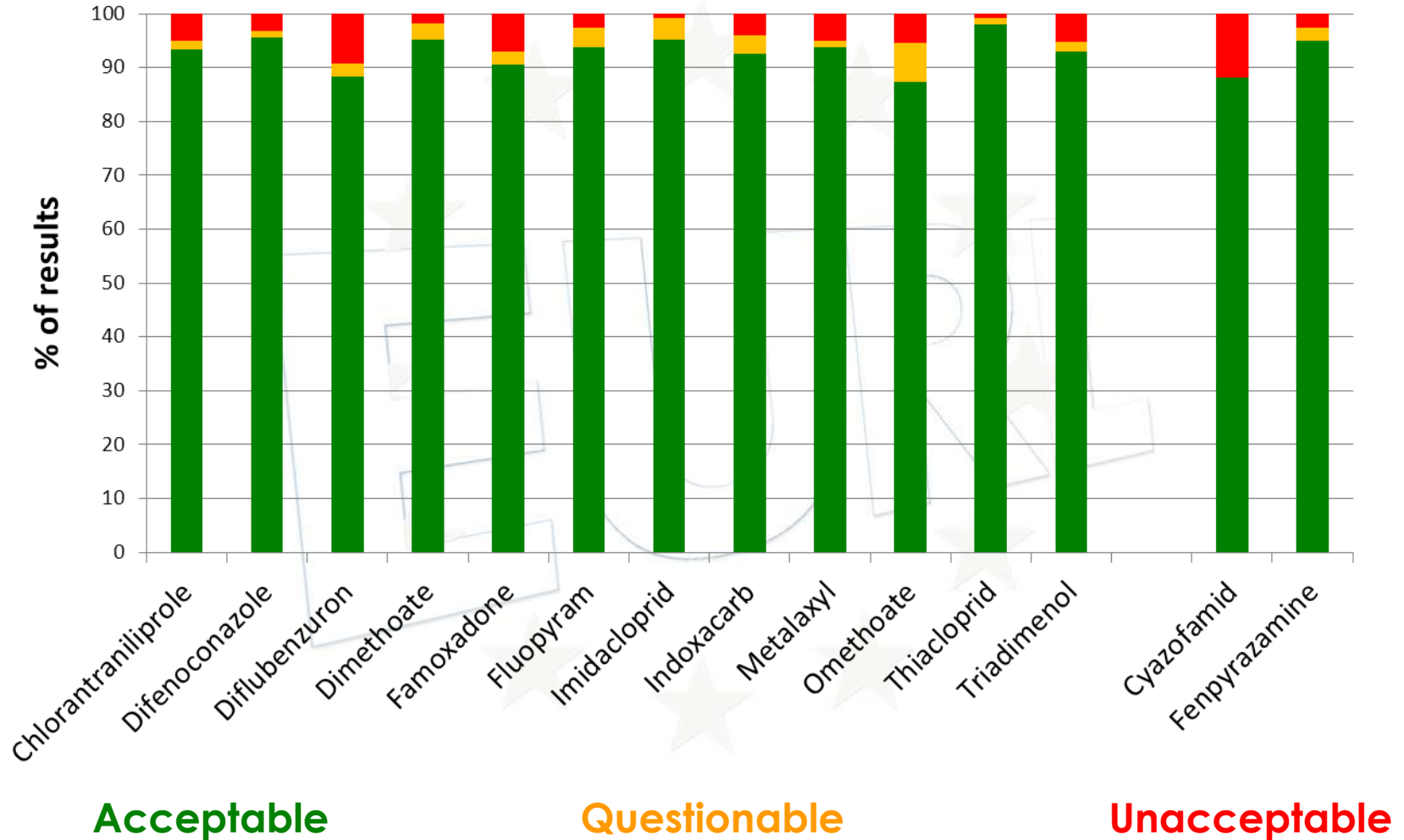


Pesticides	No. of Reported Results	No. of False Negative Results	No. of Not Analysed Results	Percentage of Labs Reporting Results (out of 171)
Chlorantraniliprole	118	2	51	69
Cyazofamid	89	3	79	52
Difenoconazole	155	2	14	91
Diflubenzuron	119	2	50	70
Dimethoate	162	3	6	95
Famoxadone	123	5	43	72
Fenpyrazamine	39	1	131	23
Fluopyram	111	3	57	65
Imidacloprid	146	1	24	85
Indoxacarb (sum of indoxacarb and its R enantiomer)	145	3	23	85
Metalaxyl and metalaxyl-M	156	3	12	91
Omethoate	147	3	21	86
Thiacloprid	144	1	26	84
Triadimenol	149	6	16	87

Pesticides	No. of Reported Results	No. of False Negative Results	No. of Not Analysed Results	Percentage of Labs Reporting Results (out of 171)
Chlorantraniliprole	118	2	51	69
Cyazofamid	89	3	79	52
Difenoconazole	155	2	14	91
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Dimethoate	162	3	6	95
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Metalaxyl and metalaxyl-M	156	3	12	91
Omethoate	147	3	21	86
Thiacloprid	144	1	26	84
Triadimenol	149	6	16	87

z scores

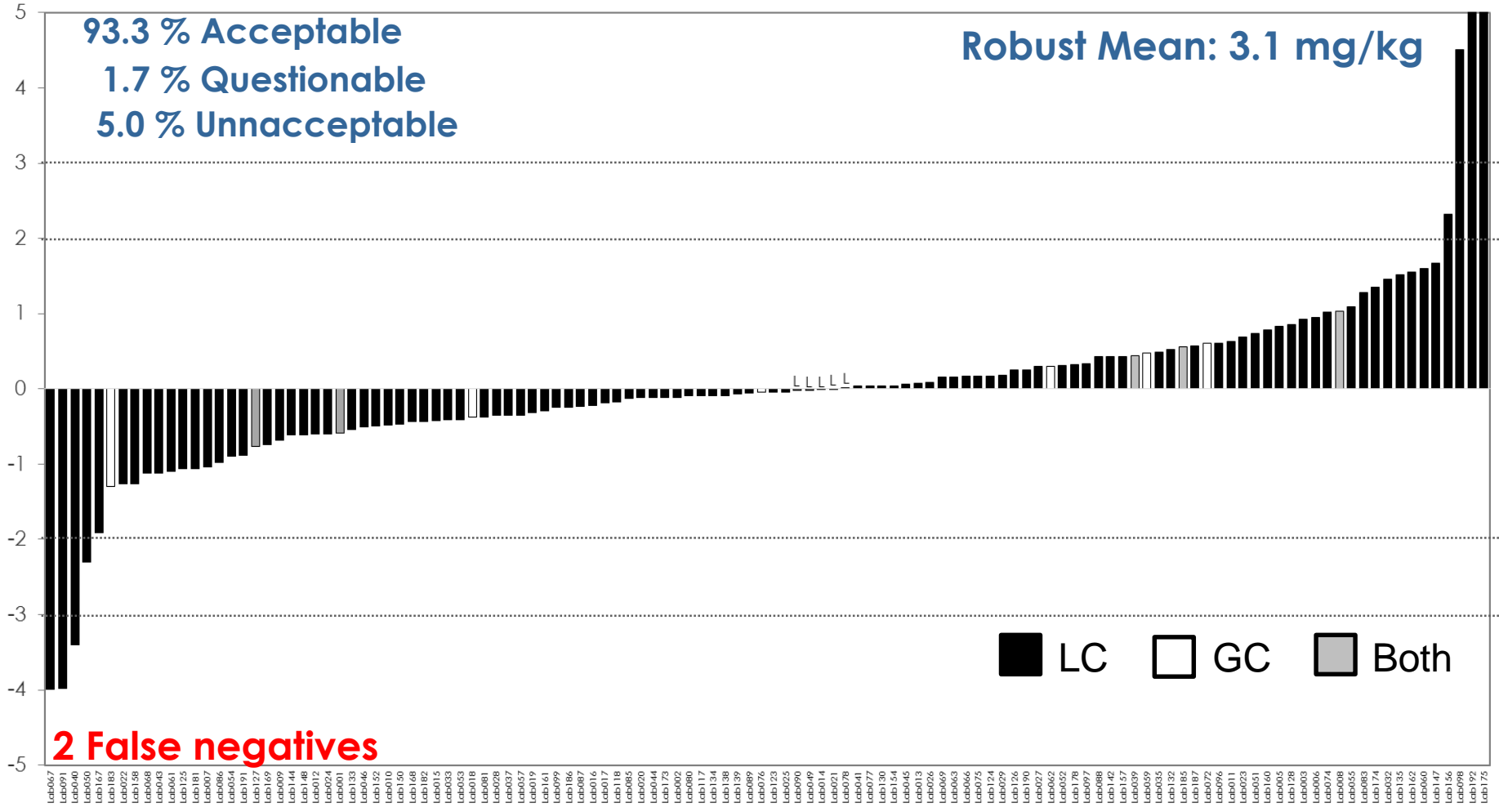
z scores classification



Pesticides	Robust Mean (mg/kg)	% Acceptable z-scores	% Questionable z-scores	% Unacceptable z-scores
Chlorantraniliprole	3.1	93.3	1.7	5.0
Difenoconazole	0.84	95.5	1.3	3.2
Cyazofamid	0.28	88.0	0.0	12.0
Diflubenzuron	1.1	88.3	2.5	9.2
Dimethoate	0.04	95.2	3.0	1.8
Famoxadone	1.0	90.6	2.4	7.1
Fenpyrazamine	0.36	95.0	2.5	2.5
Fluopyram	0.29	93.9	3.5	2.6
Imidacloprid	0.25	95.2	4.1	0.7
Indoxacarb	1.4	92.6	3.4	4.1
Metalaxyl	0.06	93.7	1.3	5.0
Omethoate	0.14	87.3	7.3	5.3
Thiacloprid	0.52	97.9	1.4	0.7
Triadimenol	0.21	92.9	1.9	5.2

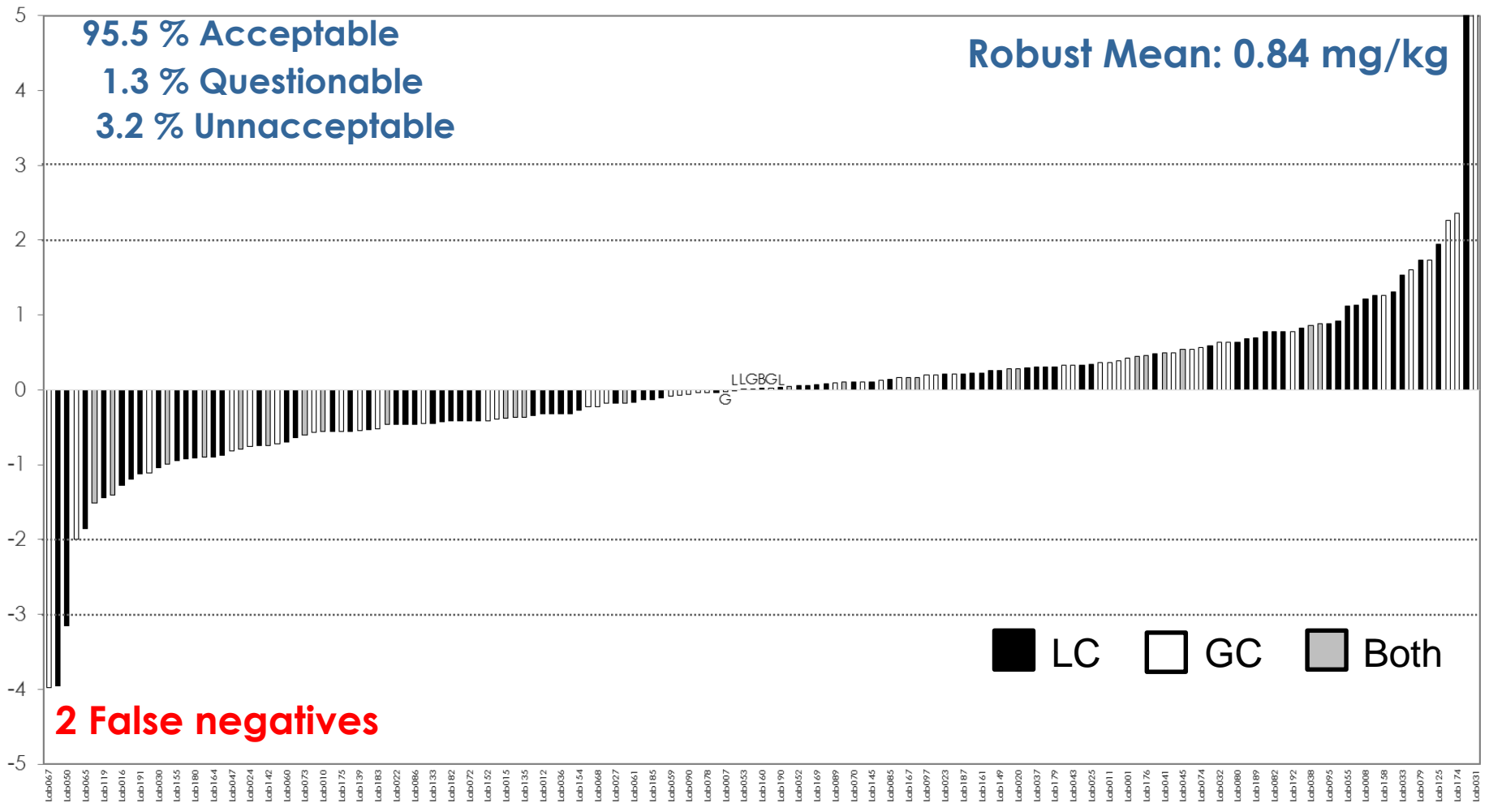
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Chlorantraniliprole



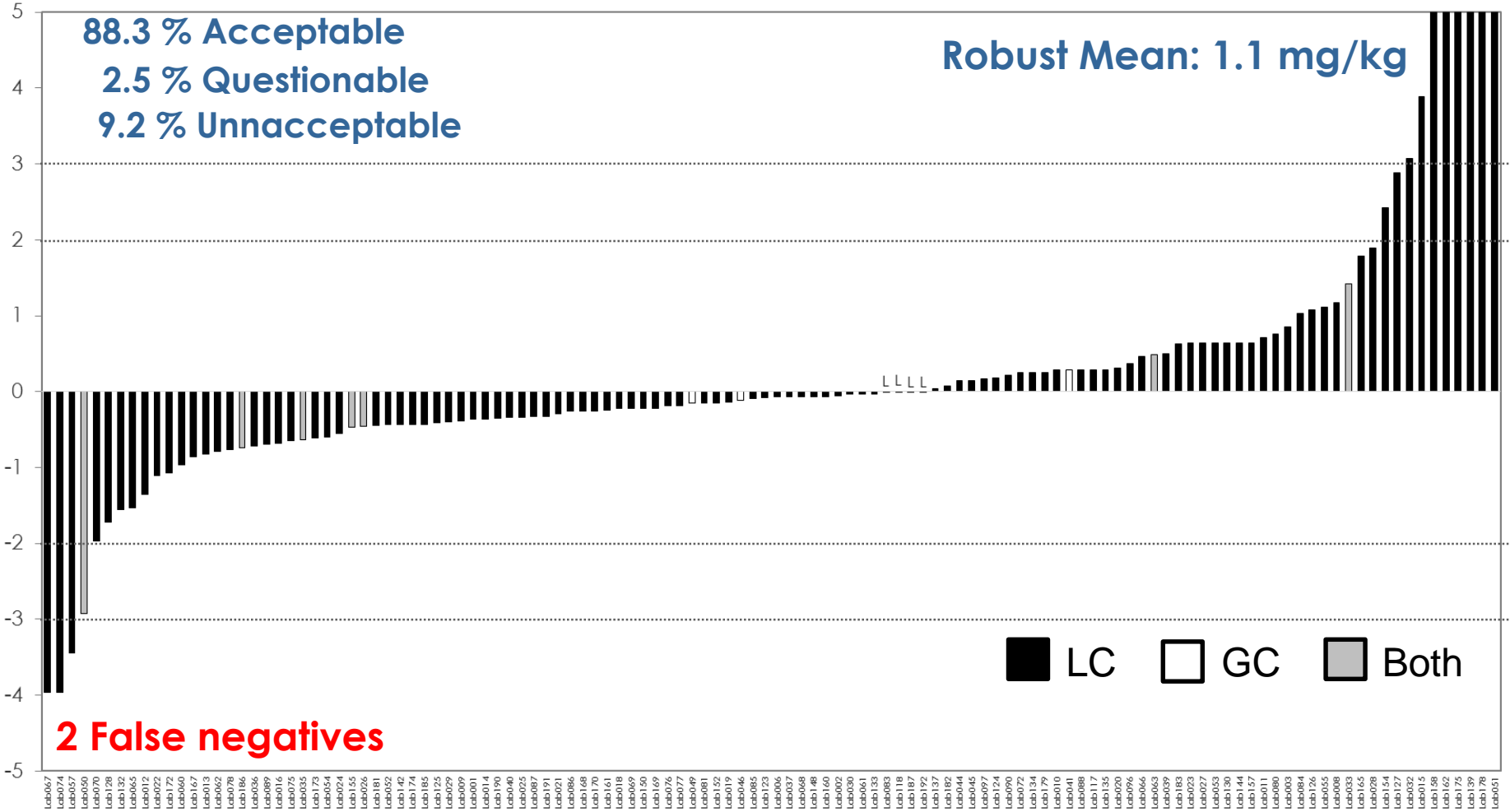
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Difenoconazole



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Diflubenzuron



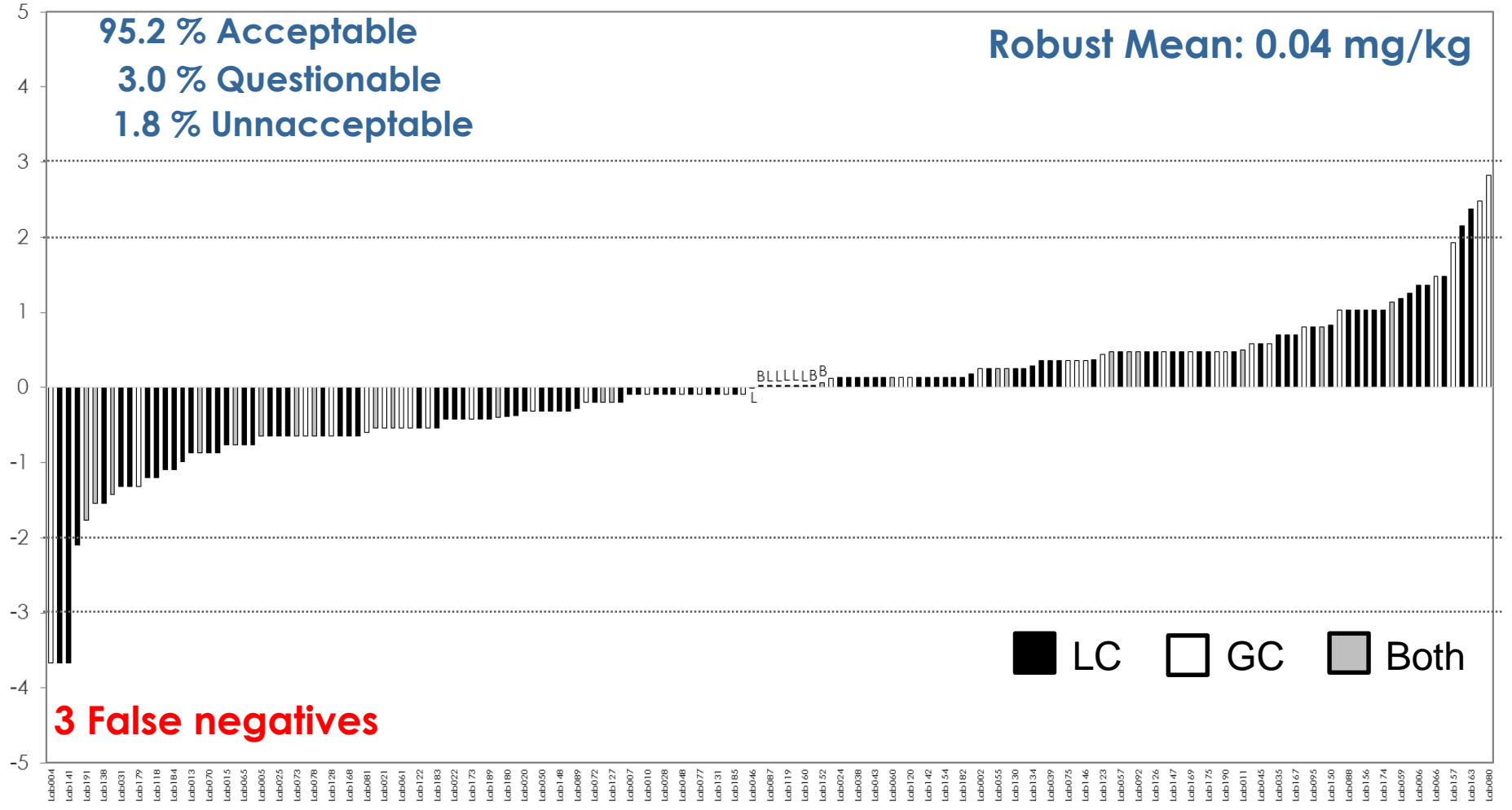


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Dimethoate

95.2 % Acceptable
 3.0 % Questionable
 1.8 % Unacceptable

Robust Mean: 0.04 mg/kg

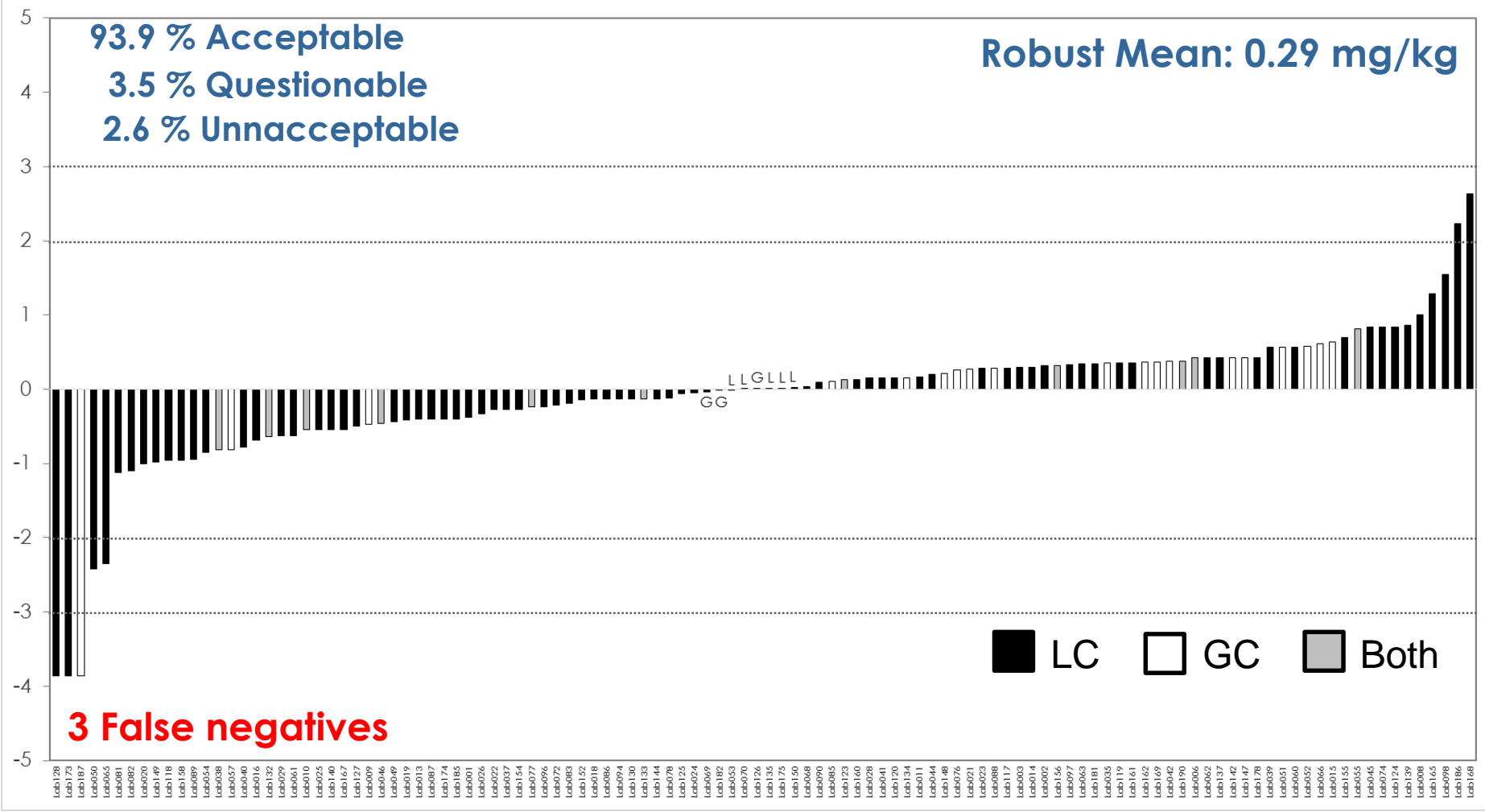


EU/EFTA Laboratories

Fluopyram

93.9 % Acceptable
3.5 % Questionable
2.6 % Unacceptable

Robust Mean: 0.29 mg/kg

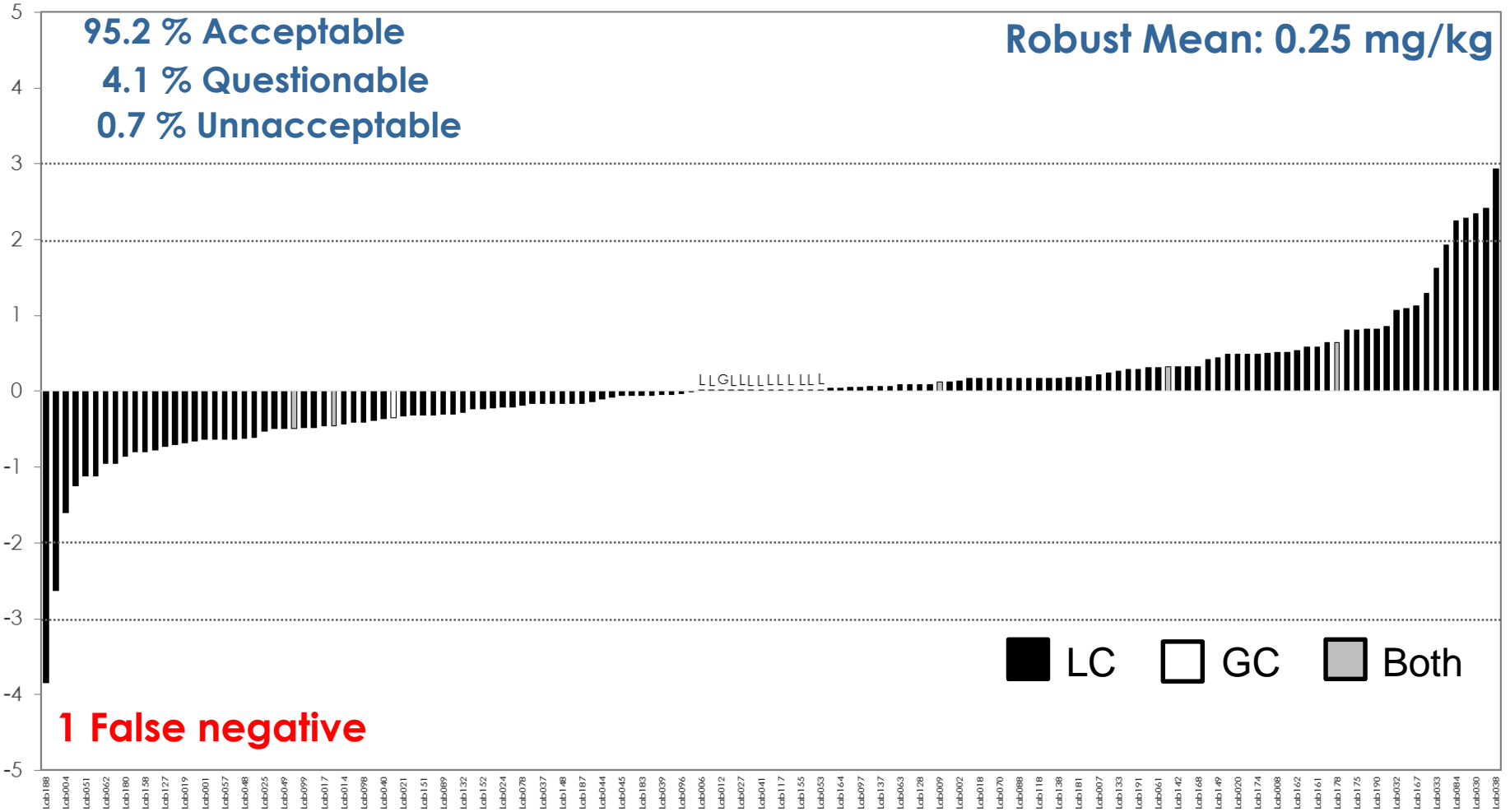


EU/EFTA Laboratories

Imidacloprid

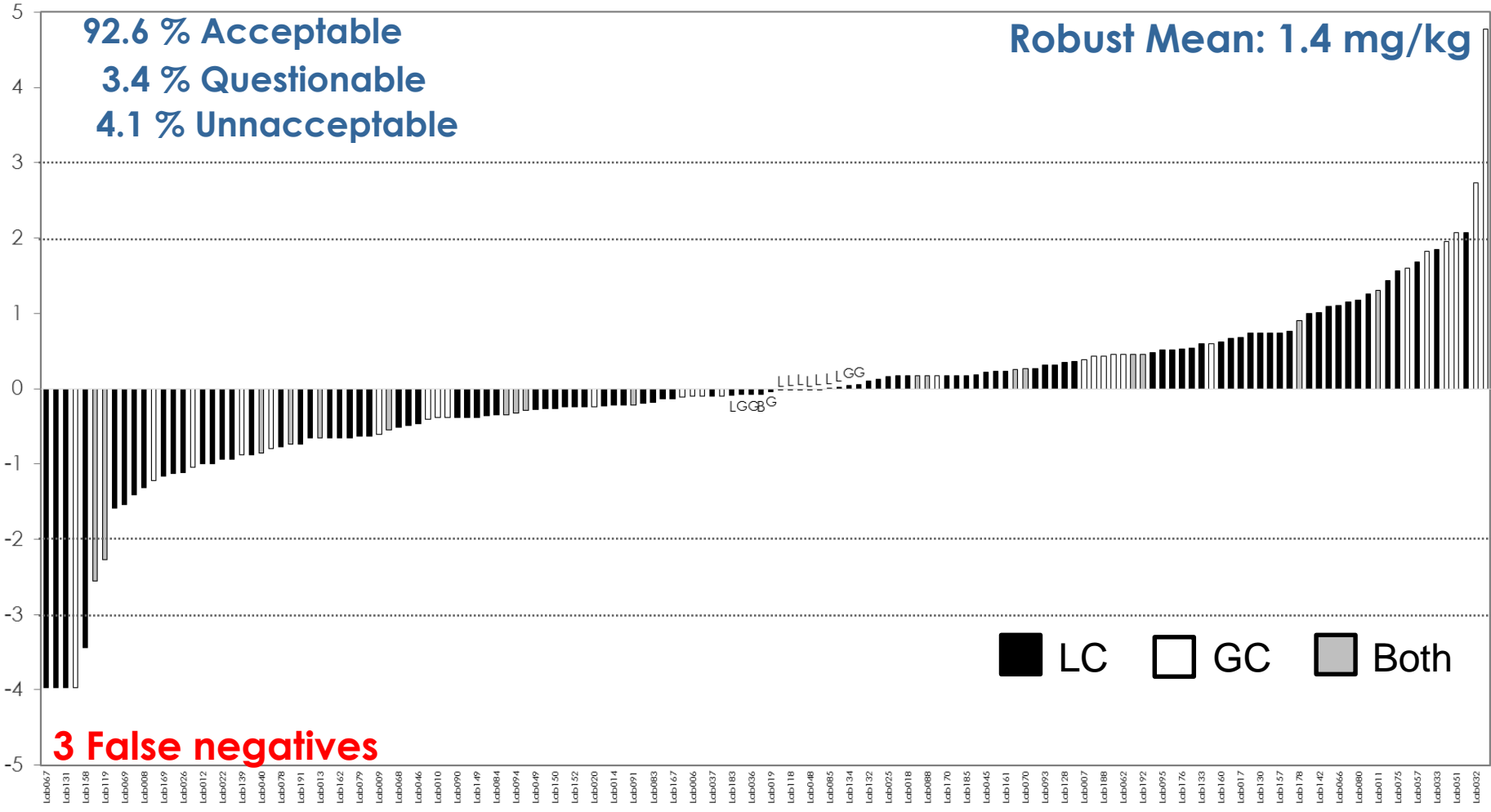
95.2 % Acceptable
4.1 % Questionable
0.7 % Unacceptable

Robust Mean: 0.25 mg/kg



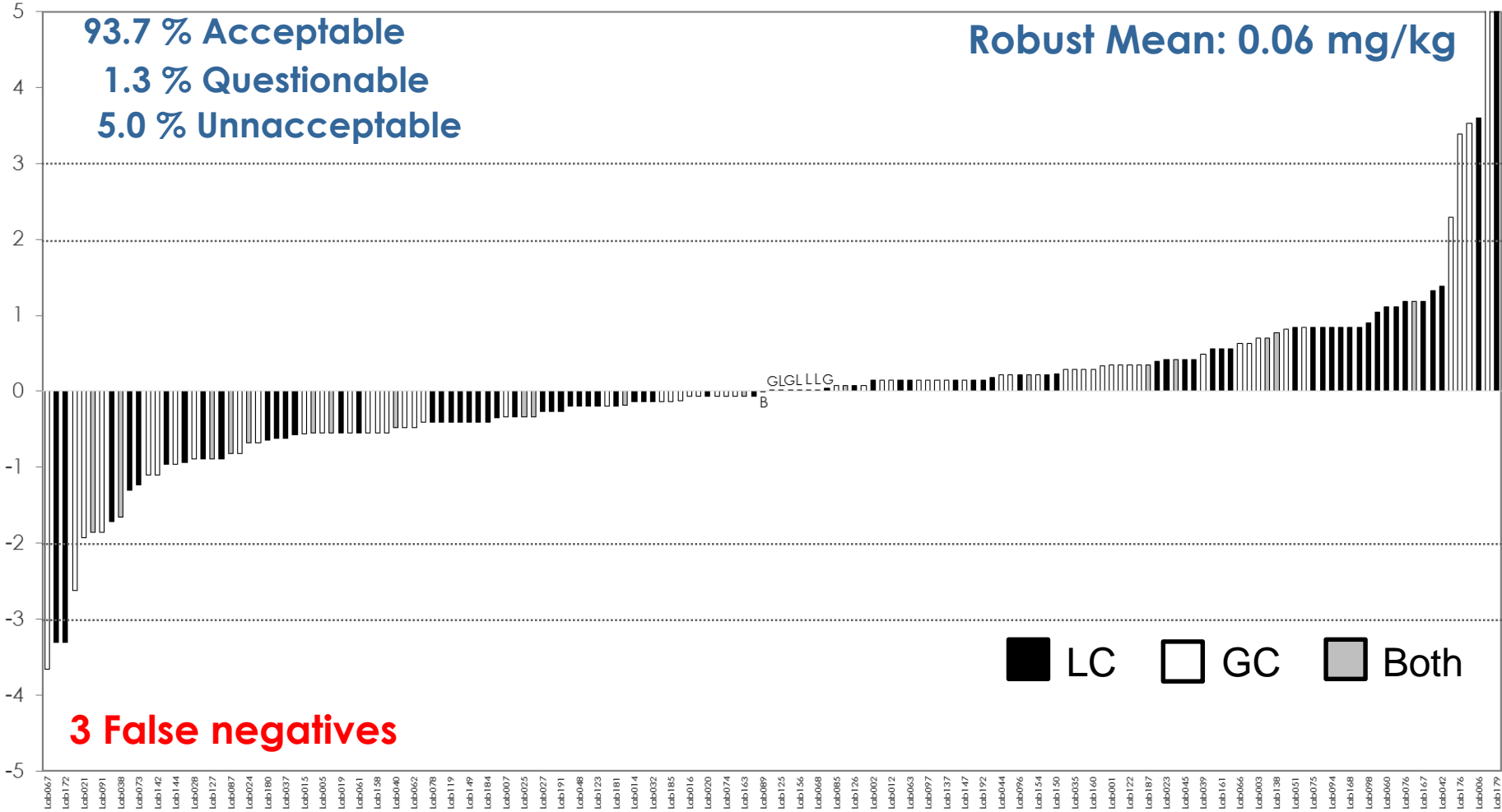
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Indoxacarb



EU/EFTA Laboratories

Metalaxyl

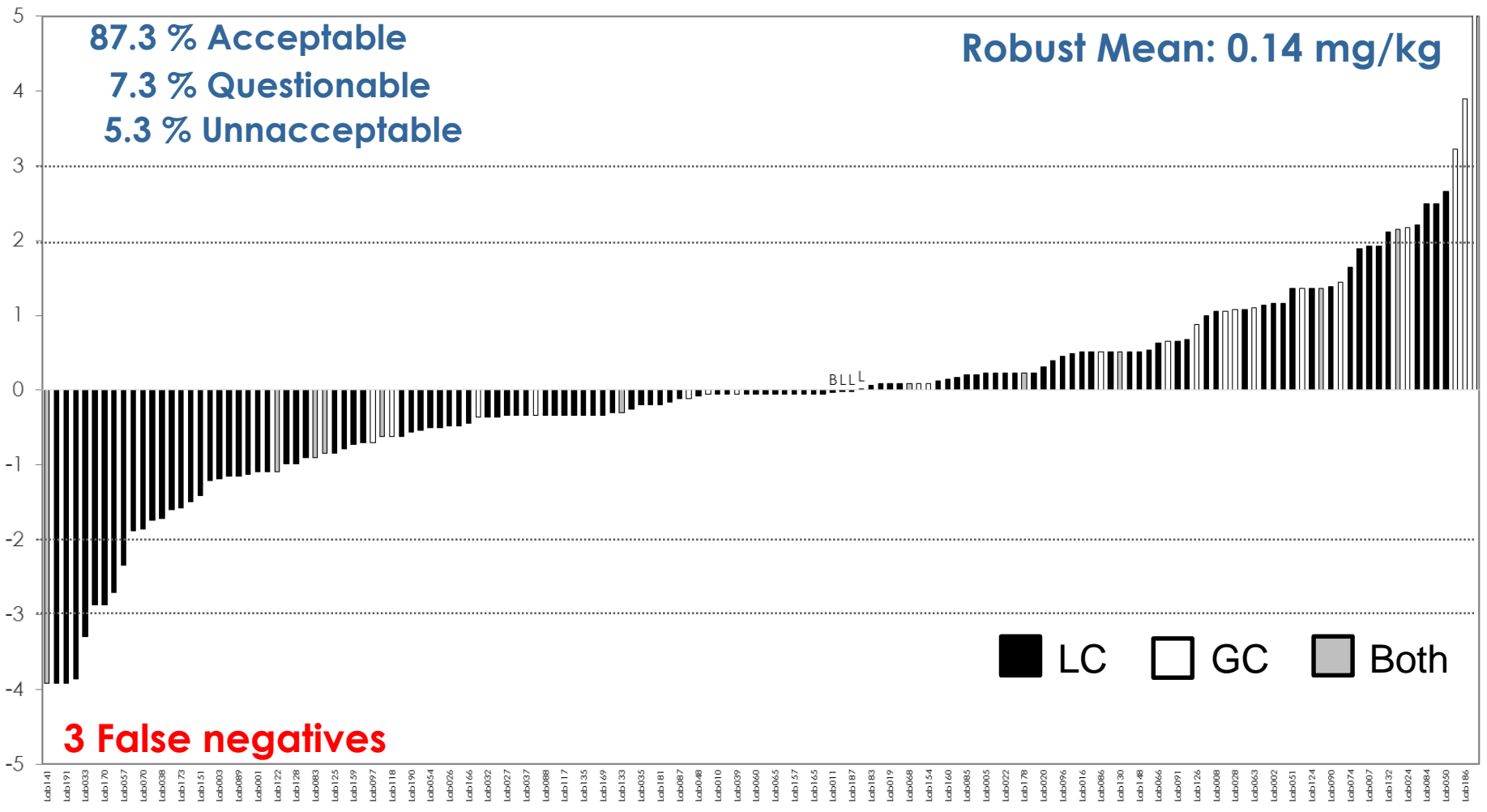


EU/EFTA Laboratories

Omethoate

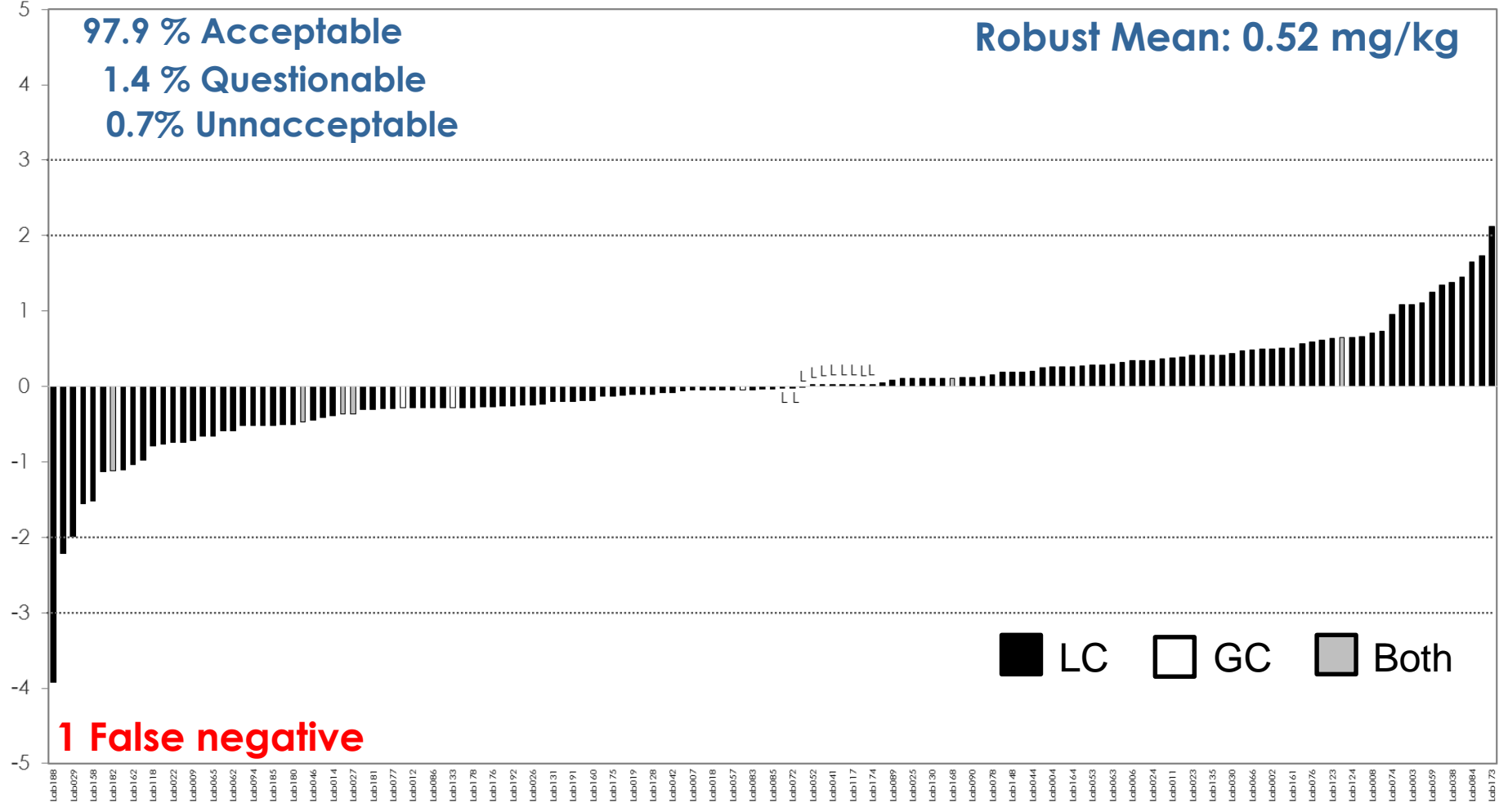
87.3 % Acceptable
7.3 % Questionable
5.3 % Unacceptable

Robust Mean: 0.14 mg/kg



EU/EFTA Laboratories

Thiacloprid



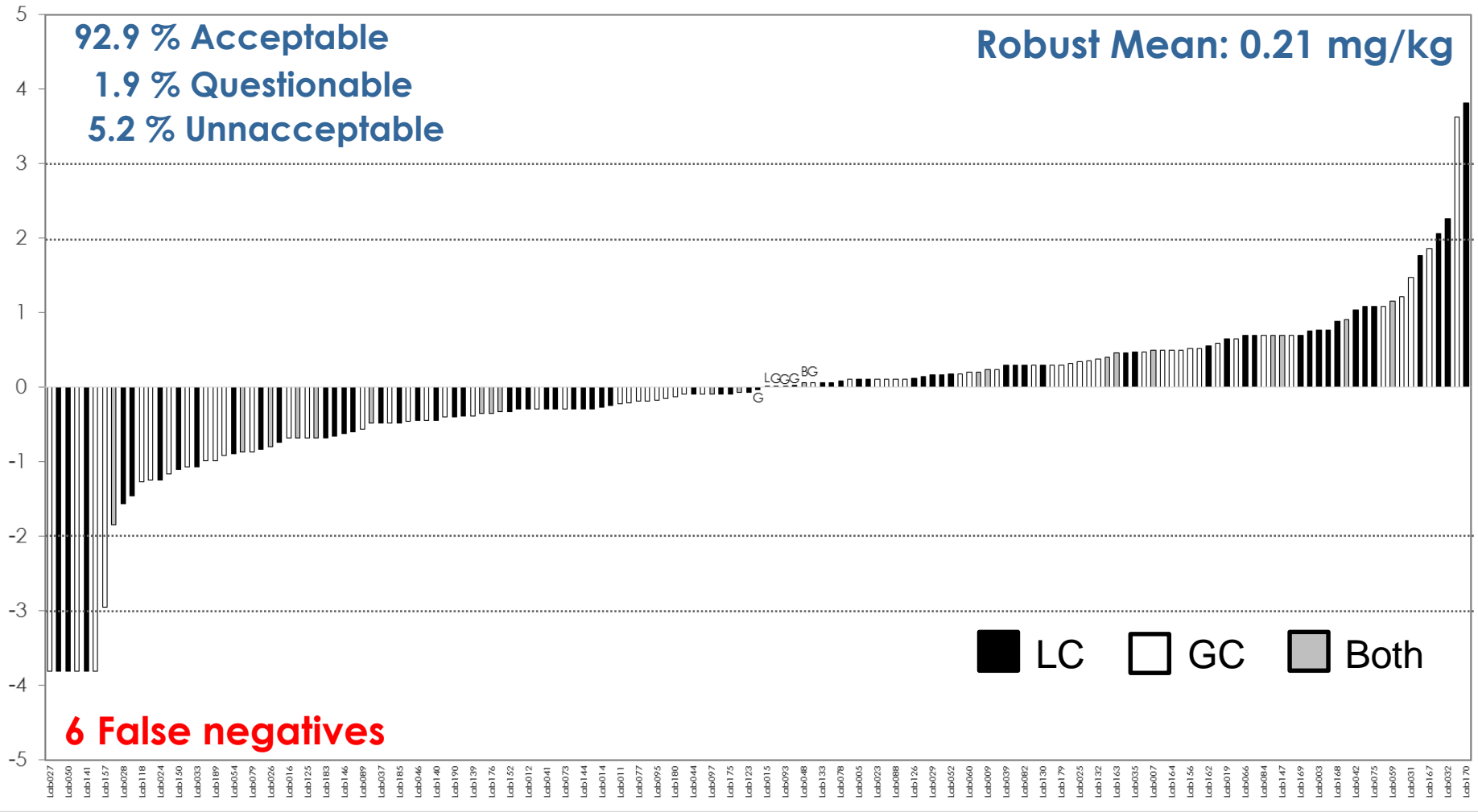


EU/EFTA Laboratories

Triadimenol

92.9 % Acceptable
1.9 % Questionable
5.2 % Unacceptable

Robust Mean: 0.21 mg/kg





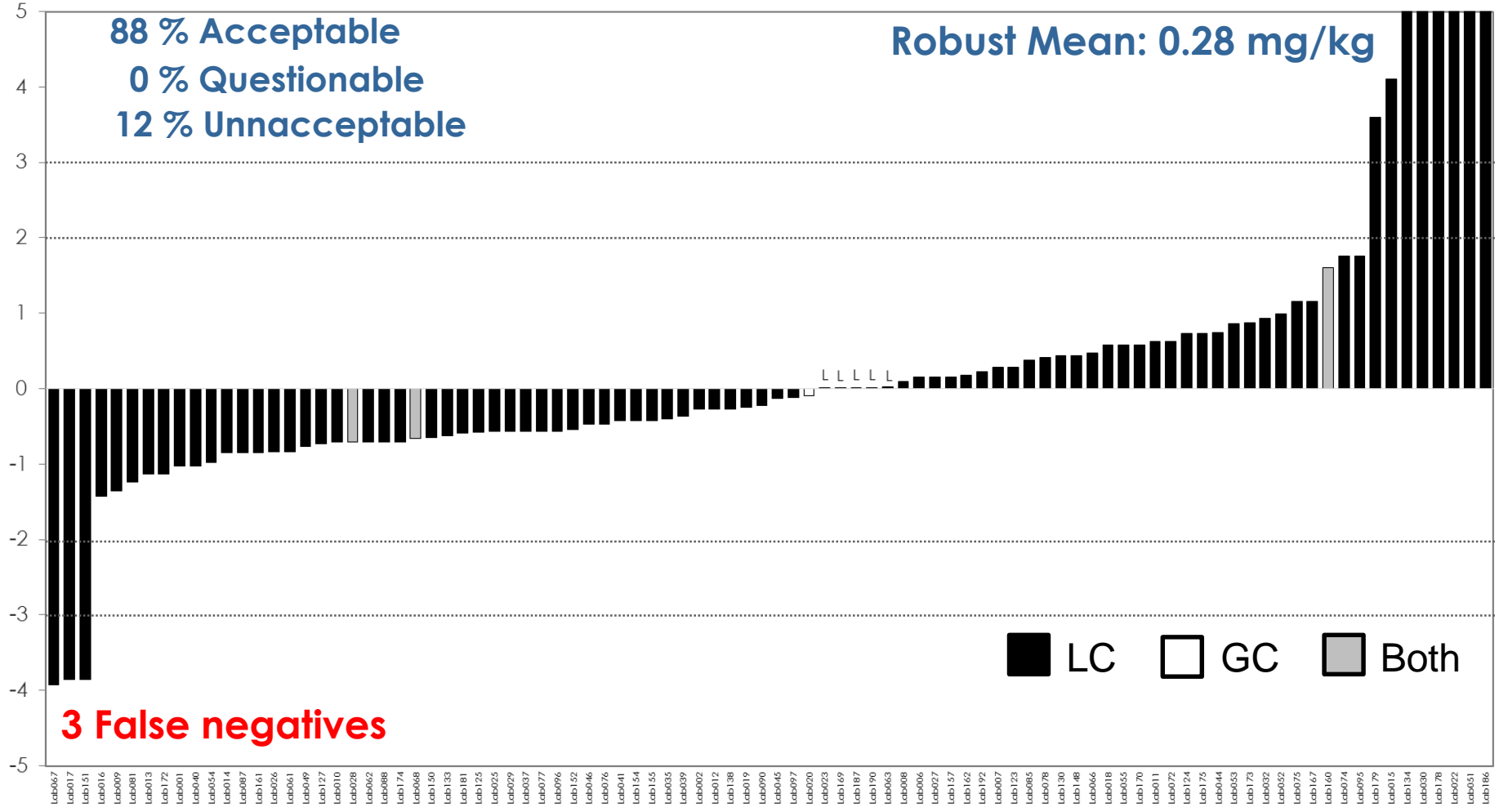
Voluntary Componds

EU/EFTA Laboratories

Cyazofamid

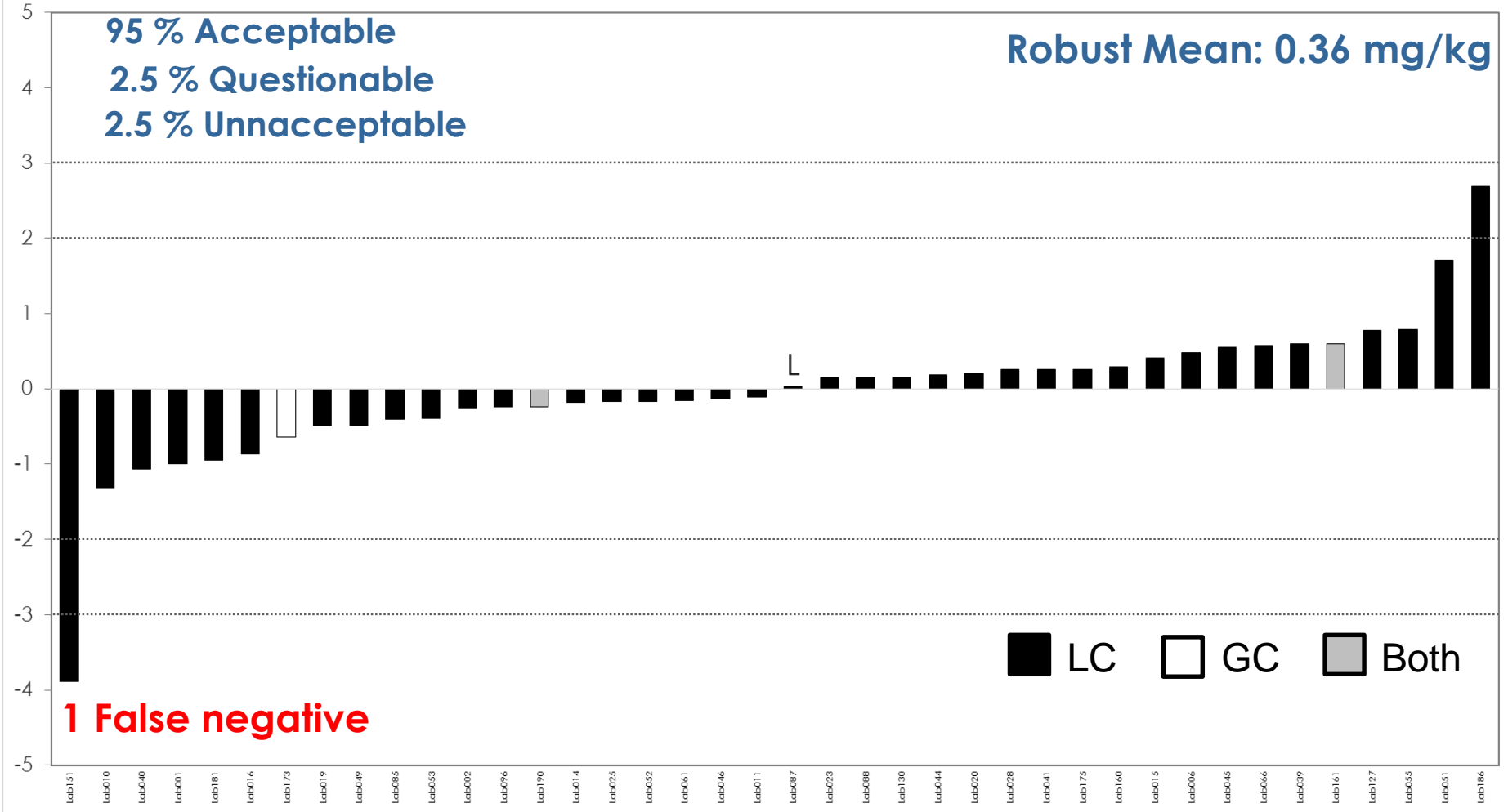
88 % Acceptable
0 % Questionable
12 % Unacceptable

Robust Mean: 0.28 mg/kg



EU/EFTA Laboratories

Fenpyrazamine



Combined z-Scores

Average of Squared z scores

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

$AZ^2 \leq 2.0$	Good
$2.0 < AZ^2 < 3.0$	Satisfactory
$AZ^2 \geq 3.0$	Unsatisfactory

Category A

Laboratories that were able to analyse at least **90% of the compulsory pesticides in the target pesticides list**, that detected and quantified at least **90 % of the pesticides present in the Test Item** and reported **no false positives**.

AZ² - Graphical Representation

■ NRL
■ OfL

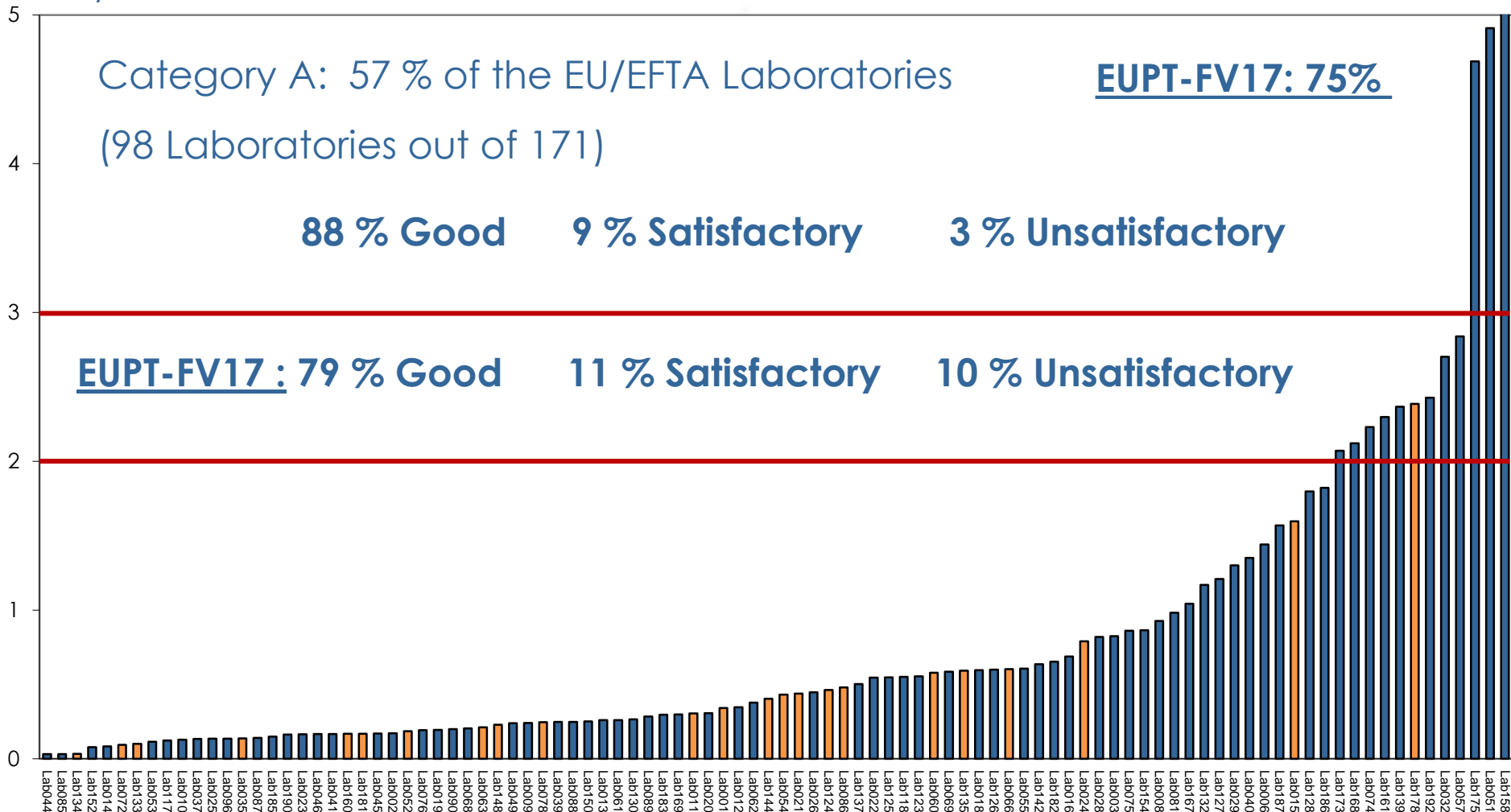
EU/EFTA Laboratories

Category A: 57 % of the EU/EFTA Laboratories
 (98 Laboratories out of 171)

EUPT-FV17: 75%

88 % Good 9 % Satisfactory 3 % Unsatisfactory

EUPT-FV17 : 79 % Good 11 % Satisfactory 10 % Unsatisfactory



False Positives

10 different laboratories from EU/EFTA countries reported **12** pesticides as false positives



Laboratory Code	Pesticide	Concentration (mg/kg)	Determination Technique	RL (mg/Kg)	MRRL (mg/Kg)
Lab164	Chlorpropham	0.513	GC-MS/MS	0.01	0.01
Lab083	Demeton-S-methylsulfone	0.043	LC-MS/MS	0.025	0.006
Lab070	Dicofol (sum of p, p' and o,p' isomers)	0.013	GC-MS/MS	0.01	0.01
Lab031	Diphenylamine	0.01	GC-MS/MS	0.01	0.01
Lab177	Endosulfan alpha	0.01	GC-ECD	0.01	0.01
Lab177	Endosulfan sulfate	0.04		0.01	0.01
Lab031	Flutolanil	0.05	GC-MS/MS	0.01	0.01
Lab047	Flutolanil	0.035	GC-MS	0.02	0.01
Lab077	Flutolanil	0.161	GC-MS/MS	0.01	0.01
Lab162	Flutolanil	0.107	GC-MS/MS	0.01	0.01
Lab042	Orthophenylphenol	0.126	GC-MS	0.01	0.01
Lab034	Triadimefon	0.21	GC-MS/MS	0.05	0.01

False Positives

GC-ECD/-MS or GC-MS/MS

- Chlorpropham
- Dicofol (sum of p, p' and o,p' isomers)
- Diphenylamine
- Endosulfan alpha
- Endosulfan sulfate
- Flutolanil
- Orthophenylphenol
- Triadimefon

LC-MS/MS

- Demeton-S-methylsulfone



Chlorantraniliprole Fluopyram Cymoxanil
Imidacloprid Cyazofamid Indoxacarb
Difenoconazole Metalaxyl Diflubenzuron
Omethoate Dimethoate Penconazole
Famoxadone Thiacloprid Fenpyrazamine
Triadimenol



Fenamiphos sulfone

Fenamiphos sulfoxide

Tetraconazole

Thiabendazole

Spiromesifen

...

Concentrations below MRRL

**Thank You
for Your Attention**



EURL EUROPEAN
UNION
REFERENCE
LABORATORY