



EUPT-FV-17
European Proficiency Test FV-17

EUPT-Panel

DG SANTE

Mrs. Almut Bitterhof

Mrs. Veerle Vanheusden

ORGANISING GROUP

Amadeo R. Fernández-Alba

Milagros Mezcua

Octavio Malato

Carmen Ferrer

STATISTICAL GROUP

Carmelo Rodríguez

QUALITY CONTROL GROUP

Antonio Valverde

Stewart Reynolds

ADVISORY GROUP

Michelangelo Anastassiades

Miguel Gamón

Magnus Jezussek

André de Kok

Ralf Lippold

Sonja Masselter

Tuija Pihlström

Mette Erecius Poulsen

Darinka Stajnbaher

Finbarr O'Regan

Philippe Gros

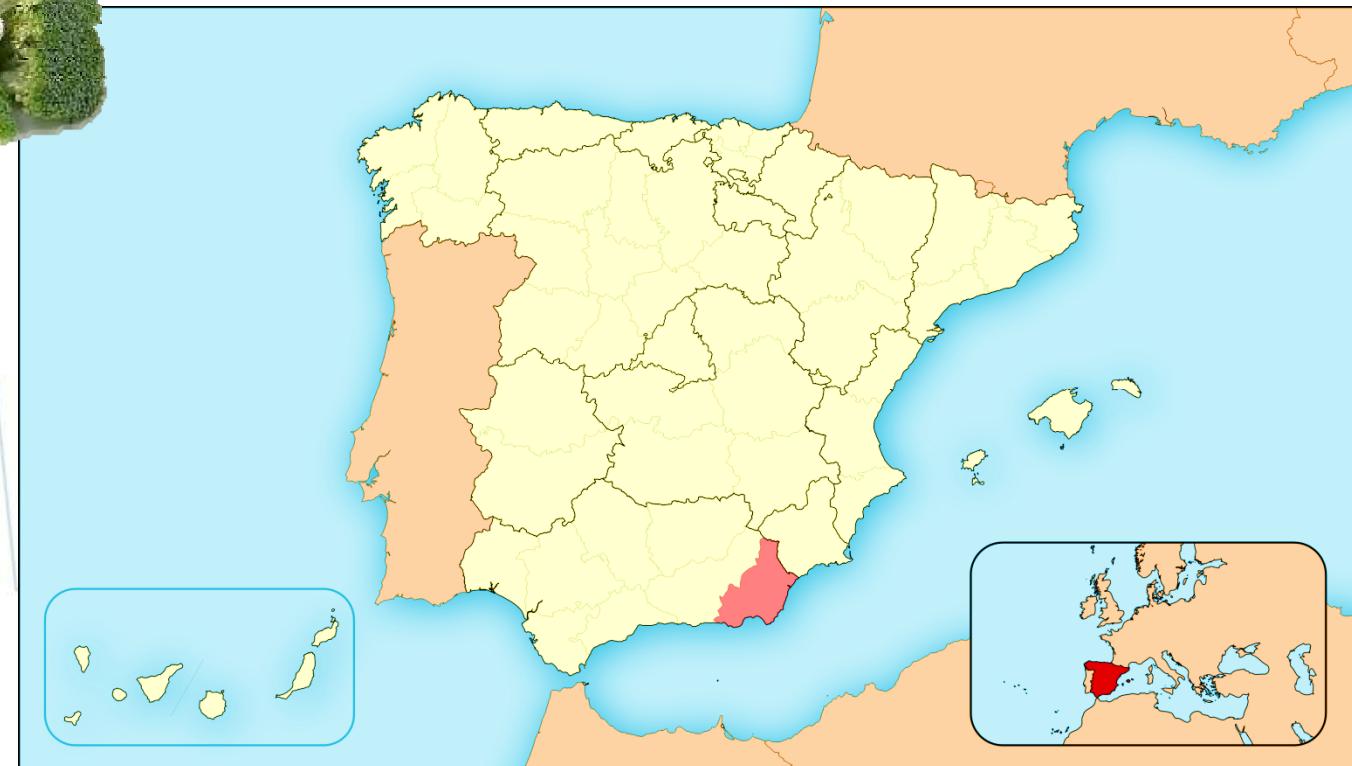
EUPT-FV-17

European Proficiency Test FV-17

Broccoli



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





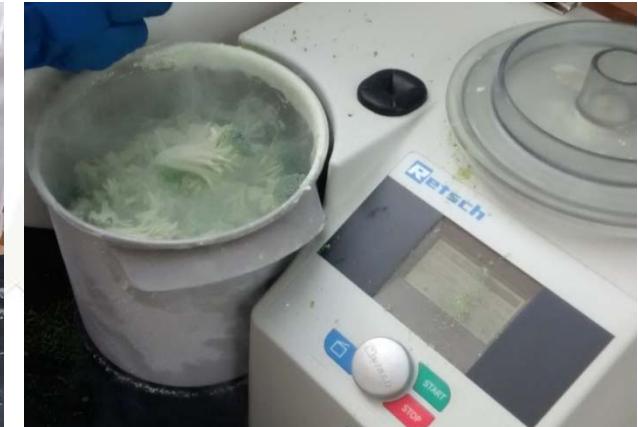
Before harvest the broccolis were treated with commercial formulations

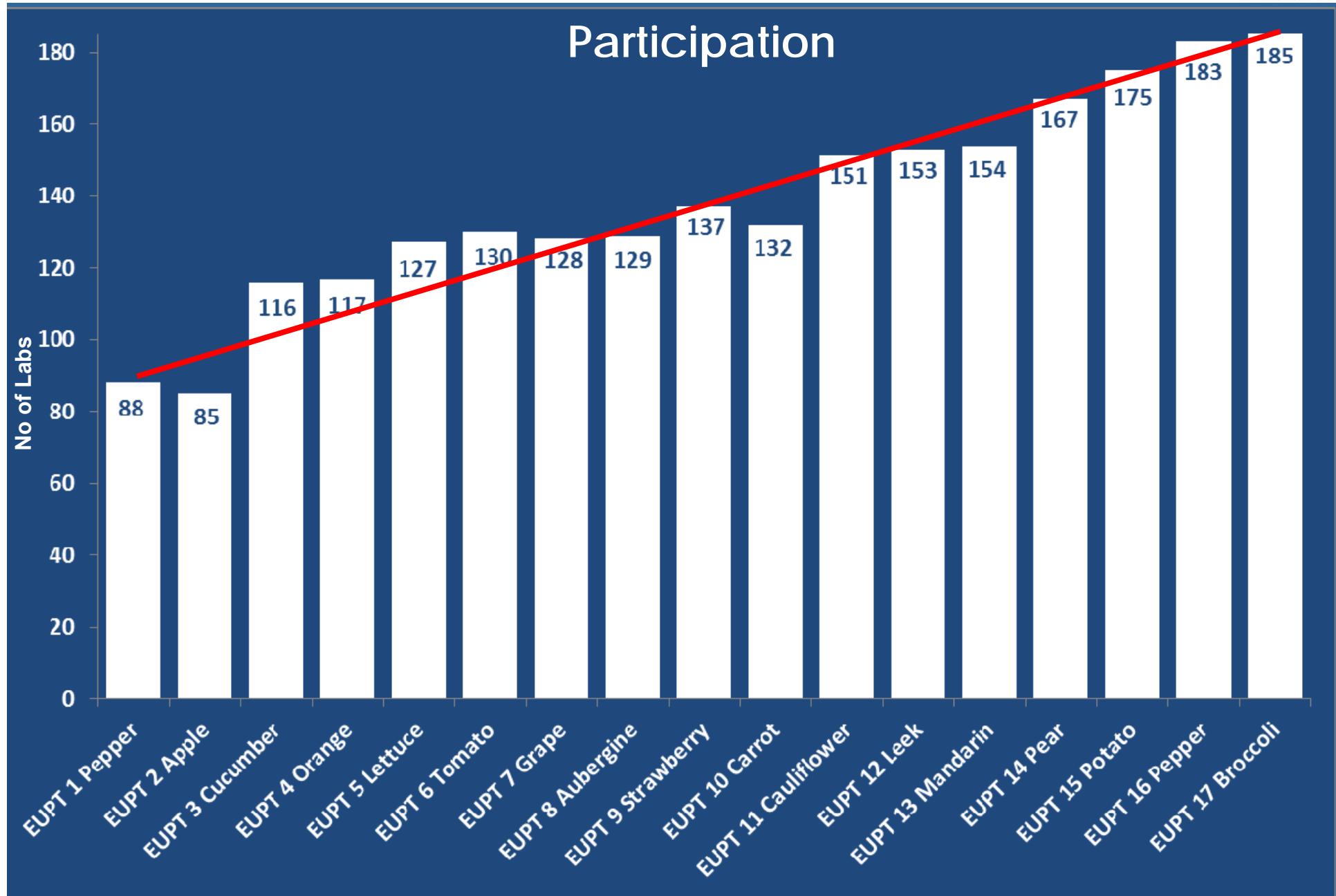


Commercial products used to treat the sample

Pesticide	Type	Commercial Product
Bupirimate	Commercial Formulation	Nimrod Quattro
Carbendazim	Commercial Formulation	Bengu 50 Flow
Diazinon	Commercial Formulation	Zoogama-D
Difenoconazole	Commercial Formulation	Core
Diflubenzuron	Commercial Formulation	Dimilin 25
Methoxyfenozide	Commercial Formulation	Runner
Pendimethalin	Commercial Formulation	Stonp LE
Permethrin	Commercial Formulation	Defendog
Spinosad	Commercial Formulation	Spintor 480 SG
Thiabendazole	Commercial Formulation	Textar 60
Trifloxystrobin	Commercial Formulation	Flint

Preparation of the test item





Country	No. of Labs	Country	No. of Labs	Country	No. of Labs
Austria	2	Hungary	4	Serbia	2
Belgium	3	Iceland	1	Singapore	1
Brazil	2	Ireland	1	Slovakia	2
Bulgaria	2	Italy	23	Slovenia	3
China	1	Jamaica	1	Spain	32
Costa Rica	1	Kenya	2	Sweden	2
Croatia	6	Latvia	1	Switzerland	2
Cyprus	1	Lebanon	1	Thailand	1
Czech Republic	3	Lithuania	1	The Netherlands	4
Denmark	2	Luxembourg	1	Turkey	1
Egypt	1	Norway	1	United Kingdom	4
Estonia	2	Peru	1	Uruguay	1
Finland	2	Poland	11	Total No. of Labs = 185	
France	7	Portugal	2	Total No. of Non-EU countries Labs = 17	
Germany	29	Romania	4	Total No. of Countries = 44	
Greece	10	Saudi Arabia	1	EU countries. EFTA countries. Other countries	

Participation

Total No. of Labs = 185

EU/EFTA Labs = 168

Other countries Labs = 17

Total No. of Countries = 44

EU/EFTA countries = 30

Other countries = 14

(27 EU + 3 EFTA + 2 Candidate countries + 12 other countries)

183 pesticides

3-hydroxy-carbofuran

Acephate

Acetamiprid

Acrinathrin

Aldicarb

Aldicarb Sulfone

Aldicarb Sulfoxide

Azinphos-methyl

Azoxystrobin

Benfuracarb

Benomyl

Bifenthrin

Bitertanol

Boscalid

Bromopropylate

Bromuconazole

Bupirimate

Buprofezin

Cadusafos

Carbaryl

Carbendazim

Carbofuran

Carbosulfan

Chlorfenapyr

Chlorfenvinphos

Chlorobenzilate

Chlorothalonil

Chlorpropham (only pa

Chlorpyrifos

Chlorpyrifos-methyl

Clofentezine (only par

Clothianidin

Cyfluthrin (cyfluthrin incl
isomers))

Cypermethrin

Cyproconazole

Cyprodinil

Deltamethrin

Demeton-S-methylsulfone

Desmethyl-pirimicarb

Diazinon

Dichlofluanid (only parent

Dichlorvos

Dicloran

Dicofol

Diethofencarb

Difenconazole

Diflubenzuron

Dimethoate

Dimethomorph

Dimethylaminosulfotoluid

Diniconazole

Diphenylamine

Endosulfan alpha

Endosulfan beta

Endosulfan sulfate

EPN

Epoxiconazole

Ethion

Ethirimol

Ethoprophos

Etofenprox

Fenamidone

Fenamiphos

Fenamiphos sulfone

Fenamiphos sulfoxide

Fenarimol

Fenazaquin

Fenbuconazole

Fenhexamid

Fenitrothion

Fenoxy carb

Fenpropothrin

Fenpropimorph

Fenpyroximate

Fenthion

Fenthion oxon

Fenthion oxon sulfone

Fenthion oxon sulfoxide

Fenthion sulfone

Fenthion sulfoxide

Fenvalerate and Esfe

Fipronil (only parent com)

Fludioxonil

Flufenoxuron

Fluopicolide

Fluopyram

Fluquinconazole

Flusilazole

Flutolanil

Flutriafol

Fosthiazate

Hexaconazole

Hexythiazox

Imazalil

Imidacloprid

Indoxacarb (Indoxacar)

Iprodione

Iprovalicarb

Isocarbophos

Isofenphos-methyl

Isoprothiolane

Kresoxim-methyl

Lambda-Cyhalothrin

Linuron

Lufenuron

Malaoxon

Malathion

Mandipropamid

Mepanipyrim (only parent c)

Metaflumizone

Metalexyl and metalaxyl-M

Metconazole

Methamidophos

Methidathion

Methiocarb

Methiocarb sulfone

Methiocarb sulfoxide

Methomyl

Methoxyfenozide

Monocrotophos

Myclobutanil

Omethoate

Orthophenylphenol

Oxadixyl

Oxamyl

Oxydemeton-methyl

Pacobutrazole

Paraoxon-methyl

Parathion-ethyl

Parathion-methyl

Penconazole

Pencycuron

Pendimethalin

Permethrin

Phenthroate

Phosalone

Phosmet

Phosmet oxon

Phoxim

Pirimicarb

Pirimiphos-methyl

Prochloraz (only parent con)

Procymidone

Profenofos

Propargite

Propiconazole

Propyzamide

Prothioconazole (Prothioconazole-destho)

Prothiofos

Pyraclostrobin

Pyridaben

Pyrimethanil

Pyriproxyfen

Quinoxifen

Spinosad (sum of spinosyn A and spinosyn

Spirodiclofen

Spiroxamine

Tau-Fluvalinate

Tebuconazole

Tebufenozyde

Tebufenpyrad

Teflubenzuron

Tefluthrin

Terbutylazine

Tetraconazole

Tetradifon

Thiabendazole

Thiacloprid

Thiamethoxam

Thiodicarb

Thiophanate-methyl

Tolclofos-methyl

Tolyfluanid

Triadimefon

Triadimenol

Triazophos

Trichlorfon (only parent compound)

Trifloxystrobin

Triflumuron

Trifluralin

Triticconazole

Vinclozolin (only parent compound)

Zoxamide

Target List

**12 New
compounds**

Pesticides used for the treatment

Bupirimate	Pendimetalin
Carbendazim	Permethrin*
Diazinon	Spinosad
Difenoconazole	Thiabendazole
Diflubenzuron	Trifloxystrobin
Methoxyfenozide	Total: 11

ALL INCLUDED IN MACP

COMMISSION IMPLEMENTING REGULATION (EU)
No 400/2014 of 22 April 2014
concerning a coordinated multiannual control
programme of the Union for 2015, 2016 and 2017 to
ensure compliance with maximum residue levels of
pesticides and to assess the consumer exposure
to pesticide residues in and on food of plant and
animal origin .

* New in the target list

Calendar

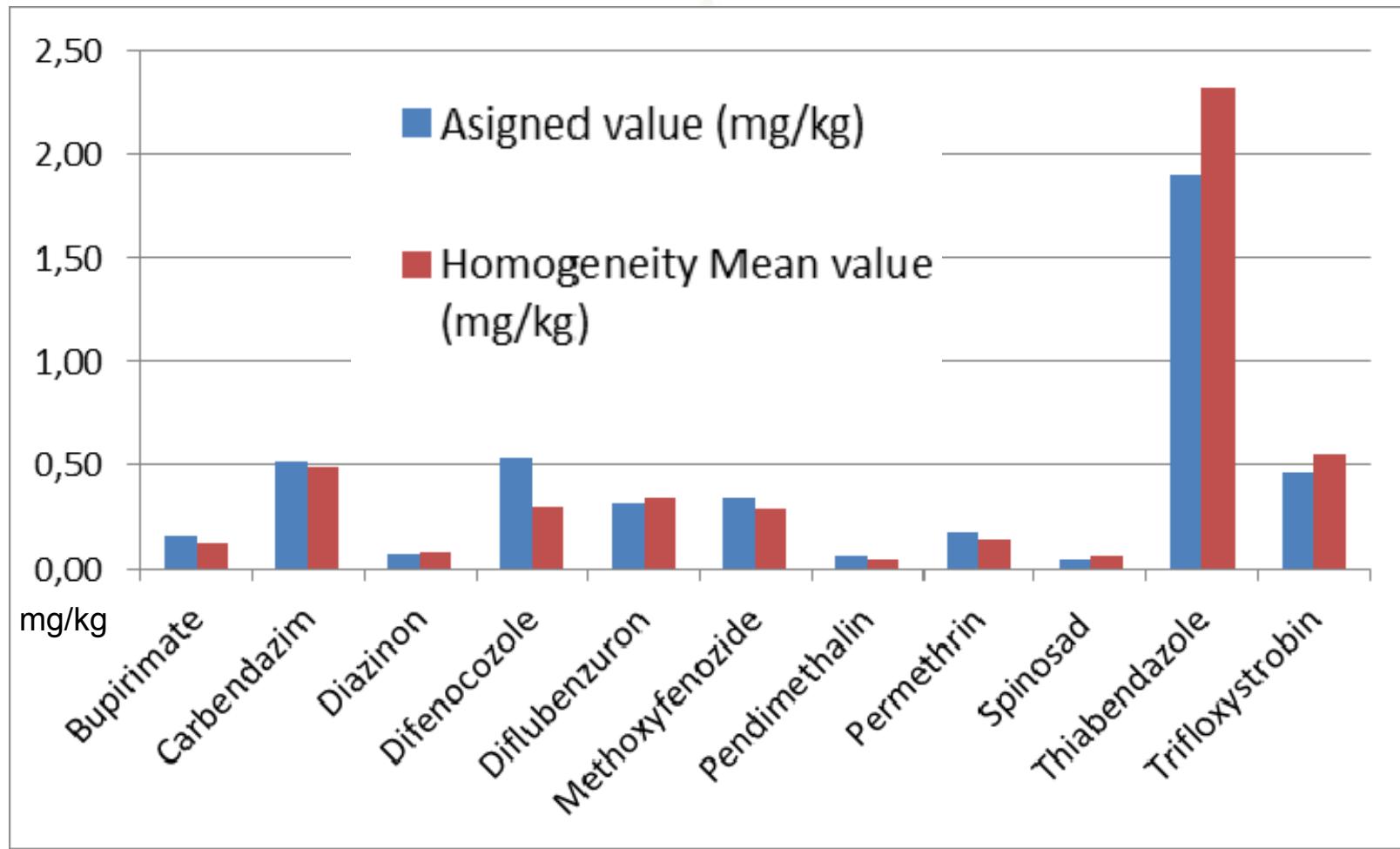
ACTIVITY	DATE
- Publishing the Target Pesticide List, Calendar and Matrix on the Web page.	15 th December 2014
- Receiving Application Form from invited laboratories.	12 th Jan-13 th Feb 2015
- Specific Protocol published on the Web site.	23 rd Feb 2015 at the latest
- Deadline for receiving Laboratory scope: Form 0	23 rd Feb-6 th March 2015
- Sample distribution.	16 th March 2015
- Deadline for receiving sample acceptance: Form 1	20 th March 2015
- Deadline for receiving results: Forms 2, 3 and 4	13 th April 2015
- Filling in Form 5	20 th -24 th April 2015
- Preliminary Report: only results, no statistical treatment.	May 2015
- Final Report distributed to the Laboratories.	December 2015

Homogeneity

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

All the pesticides passed the homogeneity test

Homogeneity



Stability

ISO 13528. Annex B



Sub-sample 1



Sub-sample 2



Sub-sample 3

Sub-sample 4

Sub-sample 5

Sub-sample 6

EURL

Stability

ISO 13528. Annex B

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

$$|x_1 - y_i| \leq 0.3 \times \sigma$$

All the pesticides passed the stability test

Results

Assigned values

Pesticides	Robust mean (mg/kg)	Uncertainty (mg/kg)
Spinosad	0.051	0.003
Pendimethalin	0.062	0.003
Diazinon	0.071	0.003
Bupirimate	0.16	0.006
Permethrin	0.17	0.007
Diflubenzuron	0.32	0.019
Methoxyfenozide	0.35	0.014
Trifloxystrobin	0.47	0.016
Carbendazim	0.51	0.023
Difenoconazole	0.53	0.016
Thiabendazole	1.90	0.071

0.051-0.100 mg/kg

Pesticides	Robust mean (mg/kg)
Spinosad	0.051
Pendimethalin	0.062
Diazinon	0.071
Bupirimate	0.16
Permethrin	0.17
Diflubenzuron	0.32
Methoxyfenozide	0.35
Trifloxystrobin	0.47
Carbendazim	0.51
Difenconazole	0.53
Thiabendazole	1.90

0.051-0.100 mg/kg

0.100-0.500 mg/kg

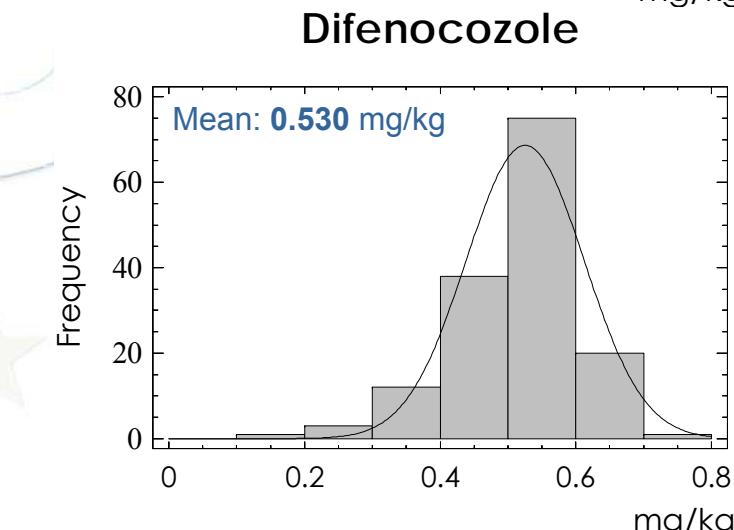
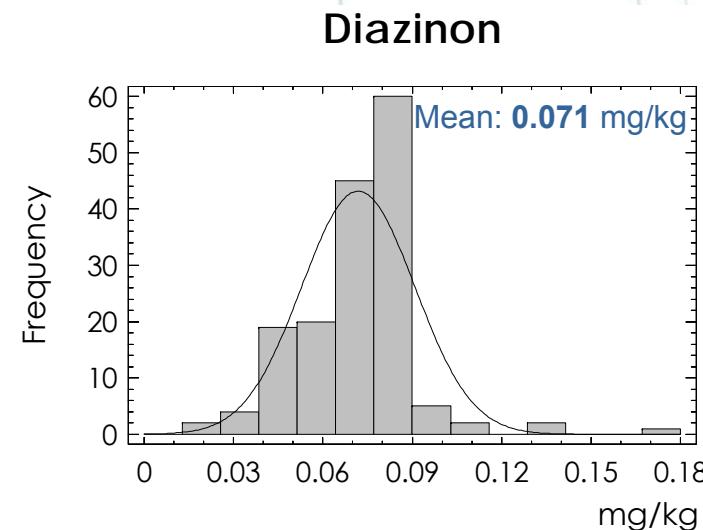
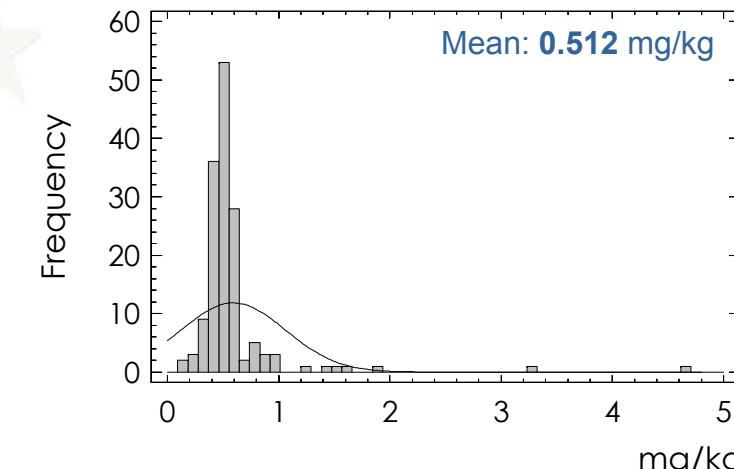
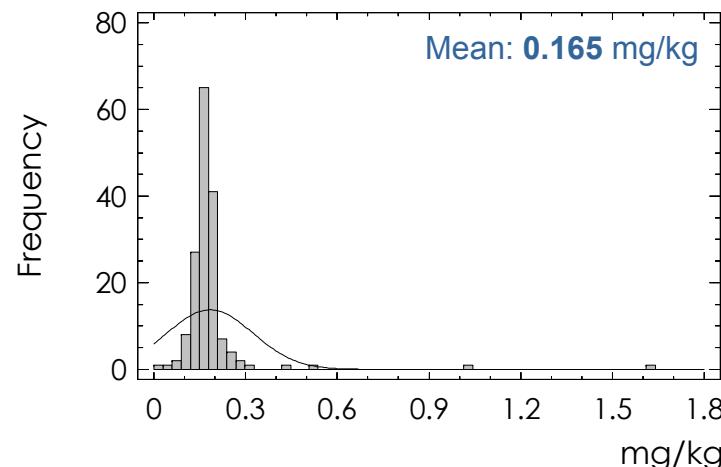
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Spinosad	0.051
Pendimethalin	0.062
Diazinon	0.071
Bupirimate	0.16
Permethrin	0.17
Diflubenzuron	0.32
Methoxyfenozide	0.35
Trifloxystrobin	0.47
Carbendazim	0.51
Difenconazole	0.53
Thiabendazole	1.90

0.051-0.100 mg/kg
0.100-0.500 mg/kg
> 0.500 mg/kg

Pesticides	Robust mean (mg/kg)
Spinosad	0.051
Pendimethalin	0.062
Diazinon	0.071
Bupirimate	0.16
Permethrin	0.17
Diflubenzuron	0.32
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Carbendazim	0.51
Difenconazole	0.53
Thiabendazole	1.90

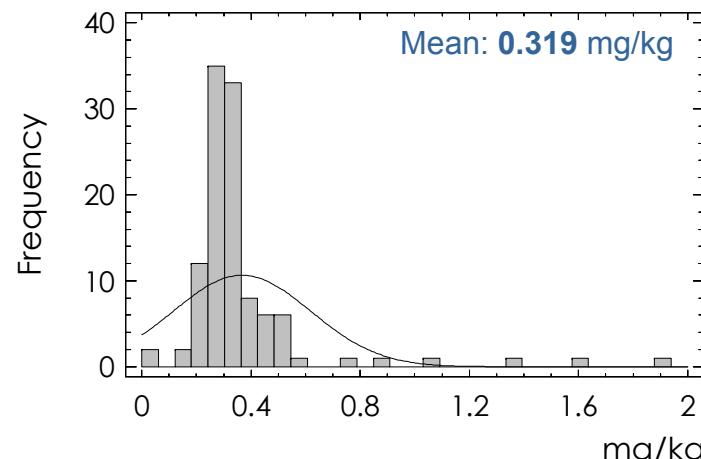
Distribution of data-Histograms

Bupirimate Carbendazim

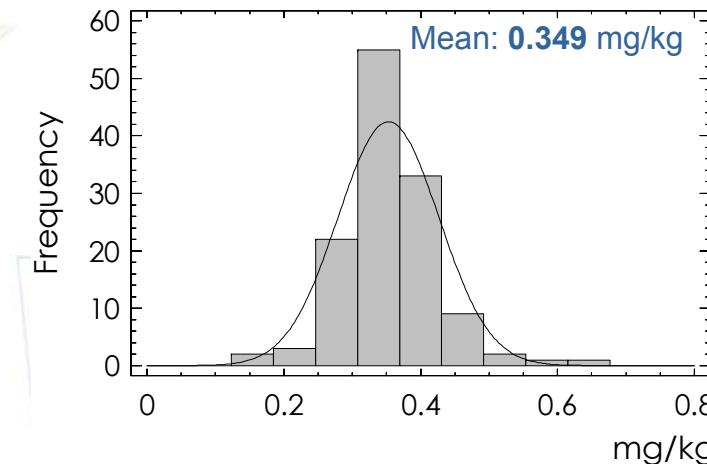


Distribution of data-Histograms

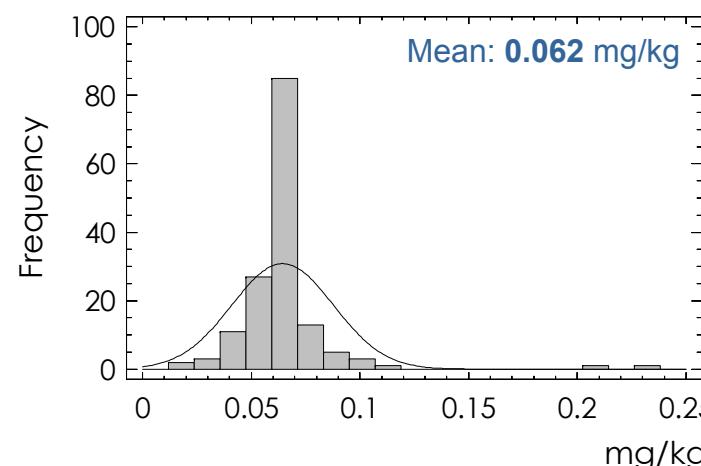
Diflubenzuron



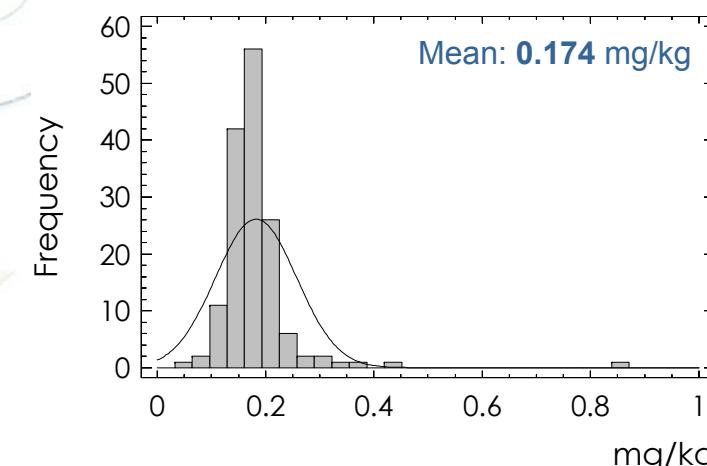
Methoxyfenozide



Pendimethalin

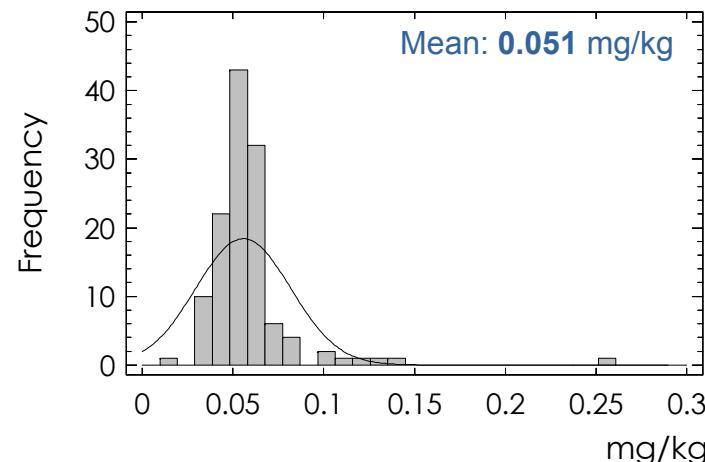


Permethrin

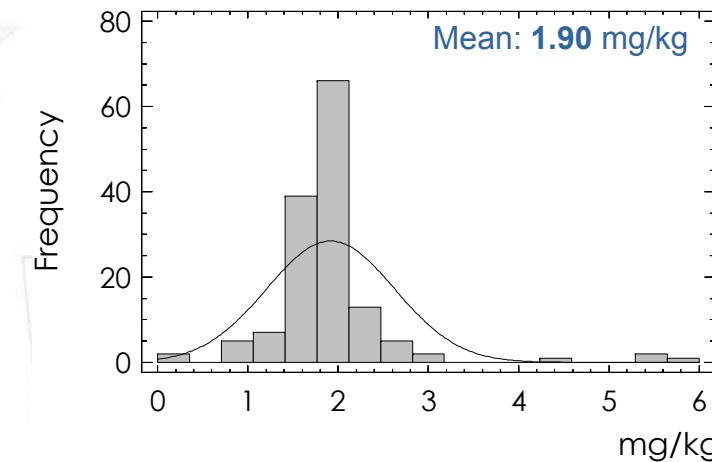


Distribution of data-Histograms

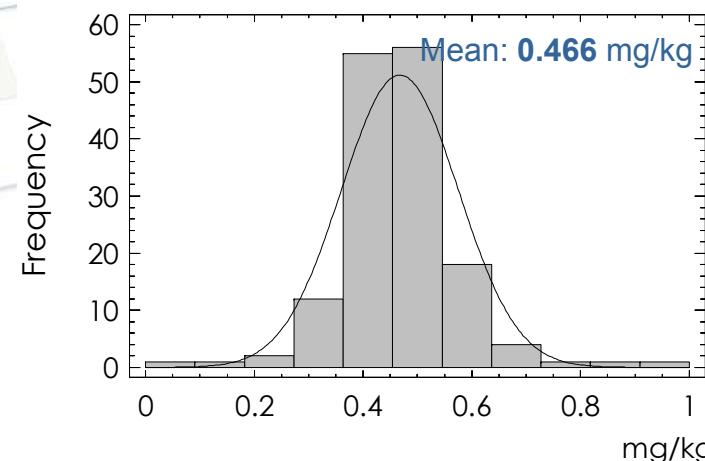
Spinosad



Thiabendazole



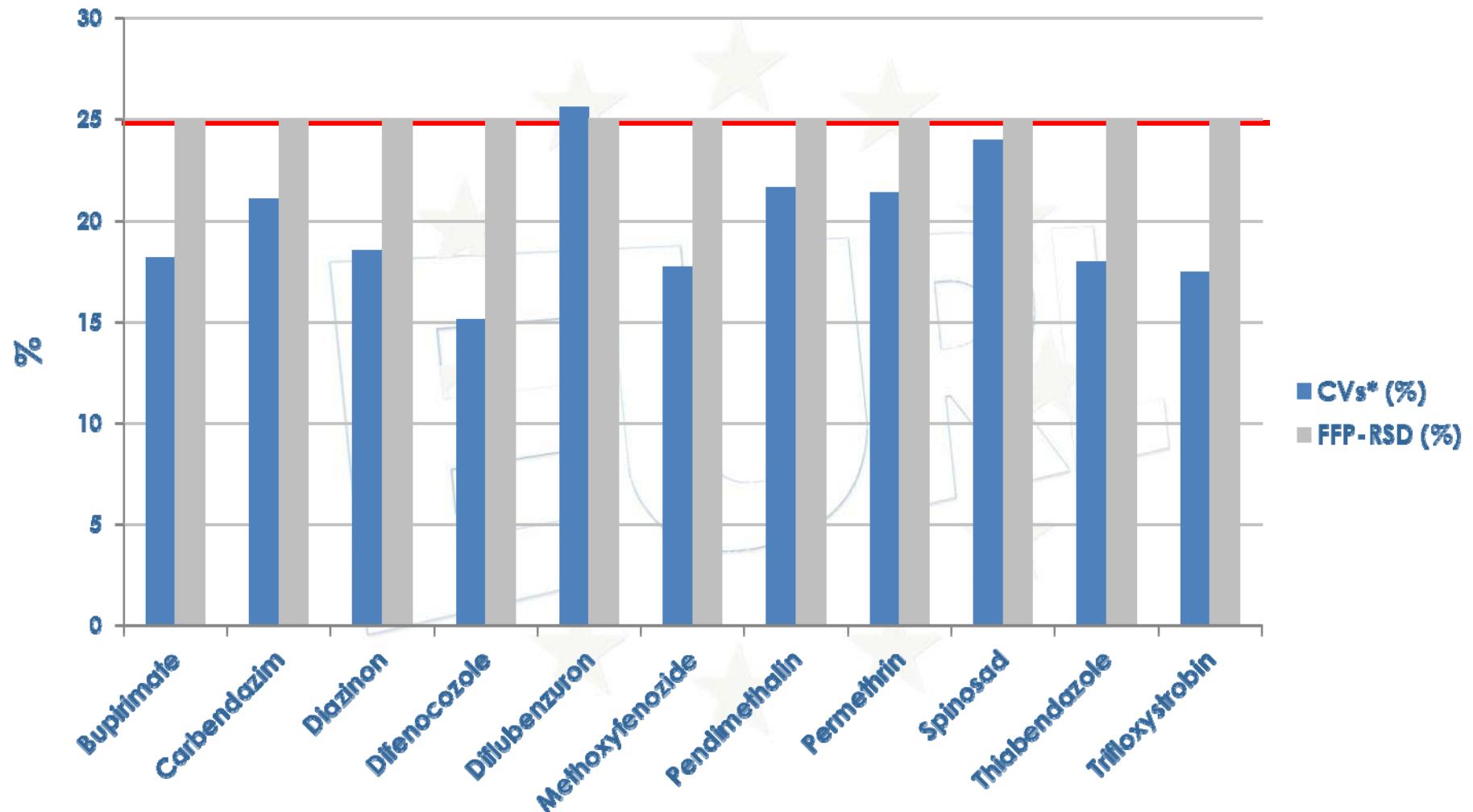
Trifloxystrobin



Dispersion of Results

Pesticides	MRRL (mg/kg)	Robust mean (mg/kg)	CV (%)
Bupirimate	0.010	0.165	18.2
Carbendazim	0.010	0.512	21.1
Diazinon	0.010	0.071	18.5
Difenoconazole	0.010	0.530	15.1
Diflubenzuron	0.010	0.319	25.6
Methoxyfenozide	0.010	0.349	17.7
Pendimethalin	0.010	0.062	21.6
Permethrin	0.010	0.174	21.4
Spinosad (sum of spinosyn A + spinosyn D, expr. as spinosad)	0.010	0.051	24.0
Thiabendazole	0.010	1.900	18.0
Trifloxystrobin	0.010	0.466	17.5

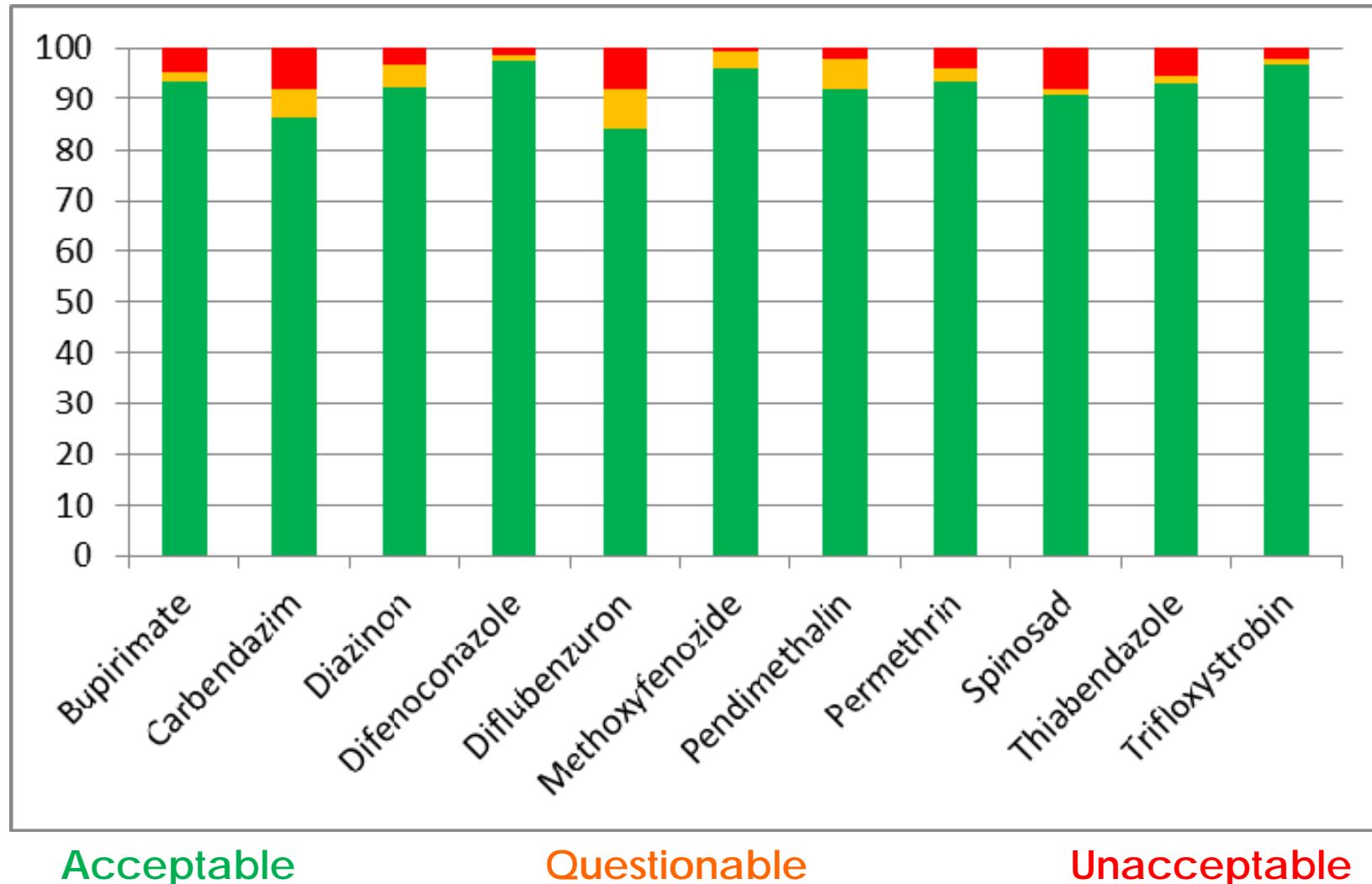
Dispersion of Results



Pesticides	No. of Reported Results	No. of False Negative Results	No. of Not Analysed Results	Percentage of Reported Results (out of 165)
Bupirimate	154	0	11	93
Carbendazim	140	0	25	85
Diazinon	160	2	3	97
Difenconazole	151	1	13	92
Diflubenzuron	111	2	52	67
Methoxyfenozide	128	0	37	78
Pendimethalin	152	1	12	92
Permethrin	152	1	12	92
Spinosad	125	2	38	76
Thiabendazole	143	2	20	87
Trifloxystrobin	152	0	13	92

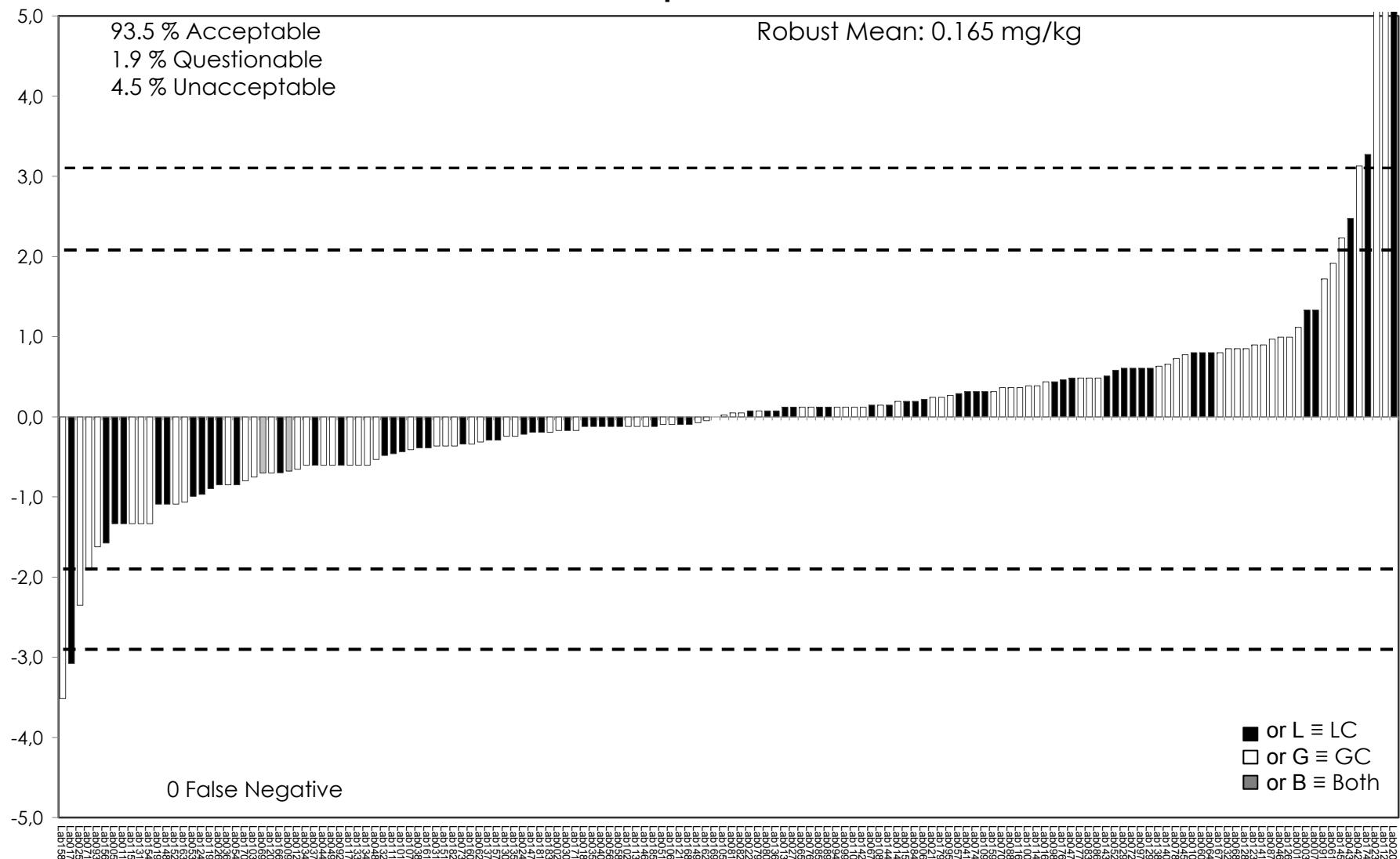
z-Scores

z-Scores classification

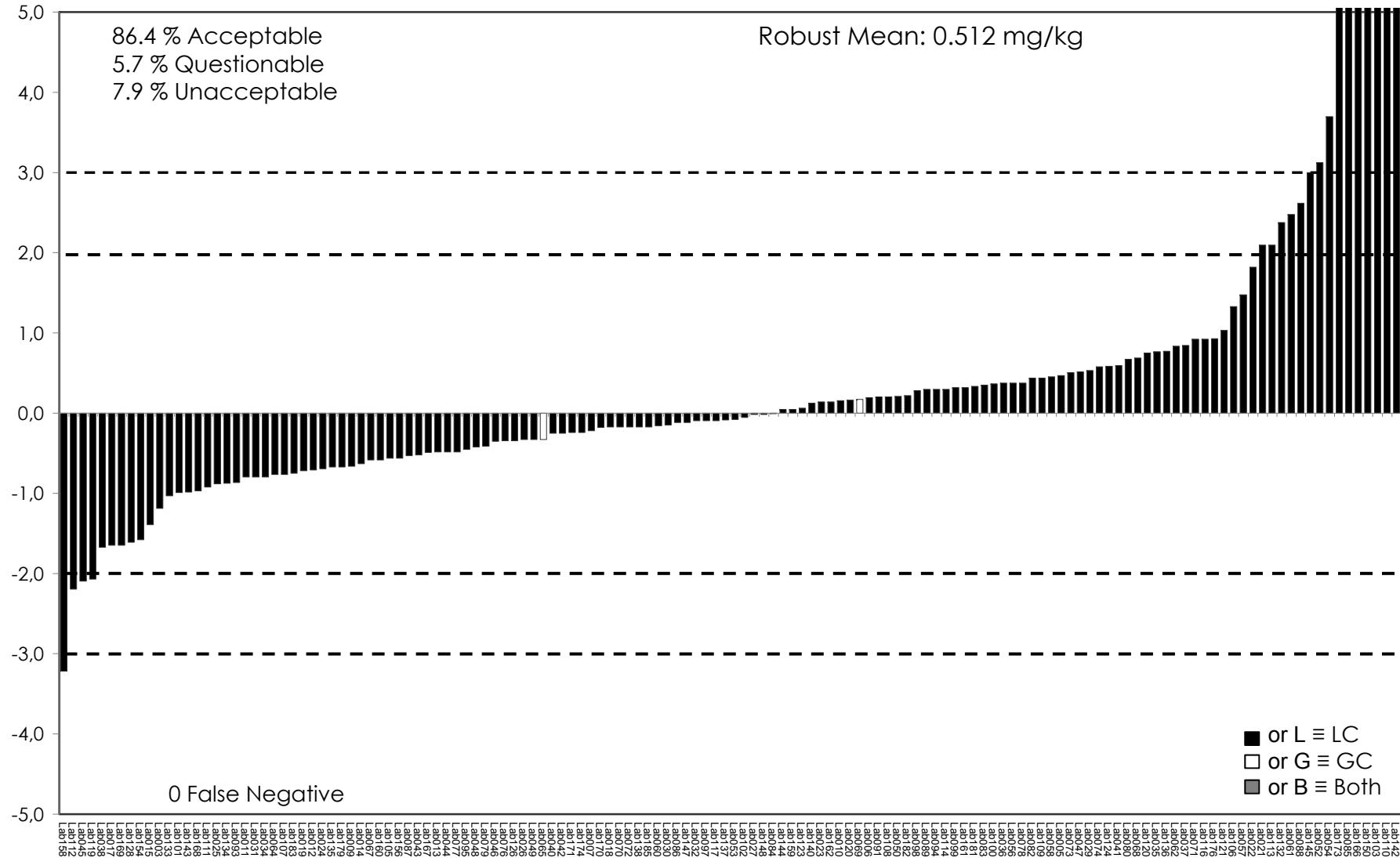


Pesticides	Robust Mean (mg/kg)	% Acceptable z-scores	% Questionable z-scores	% Unacceptable z-scores
Bupirimate	0.165	93.5	1.9	4.5
Carbendazim	0.512	86.4	5.7	7.9
Diazinon	0.071	92.6	4.3	3.1
Difenoconazole	0.530	97.4	1.3	1.3
Diflubenzuron	0.319	84.1	8.0	8.0
Methoxyfenozide	0.349	96.1	3.1	0.8
Pendimethalin	0.062	92.2	5.9	2.0
Permethrin	0.174	93.5	2.6	3.9
Spinosad (sum of spinosyn A + spinosyn D. expr. as spinosad)	0.051	90.6	1.6	7.9
Thiabendazole	1.900	93.1	1.4	5.5
Trifloxystrobin	0.466	96.7	1.3	2.0

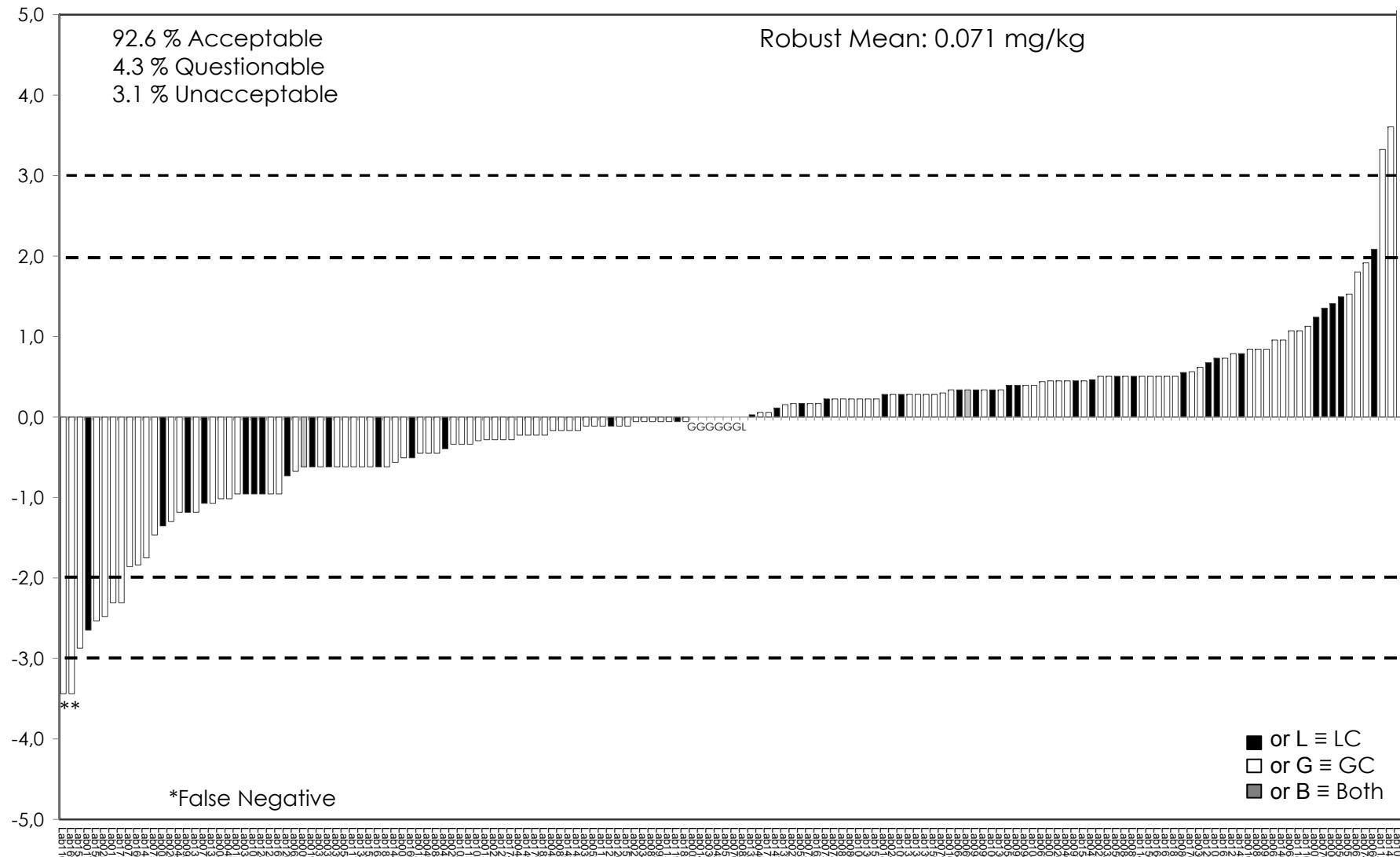
Bupirimate



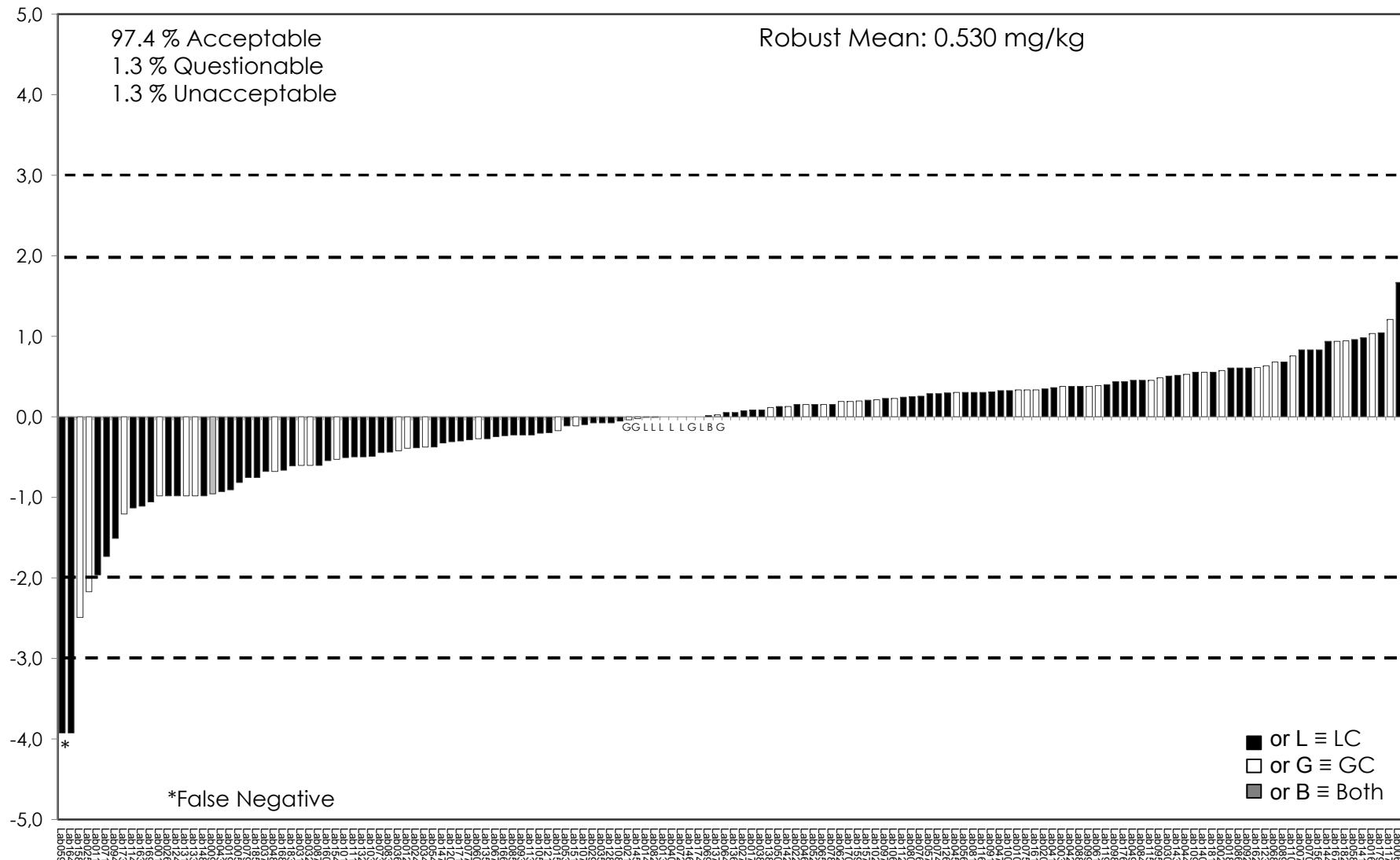
Carbendazim



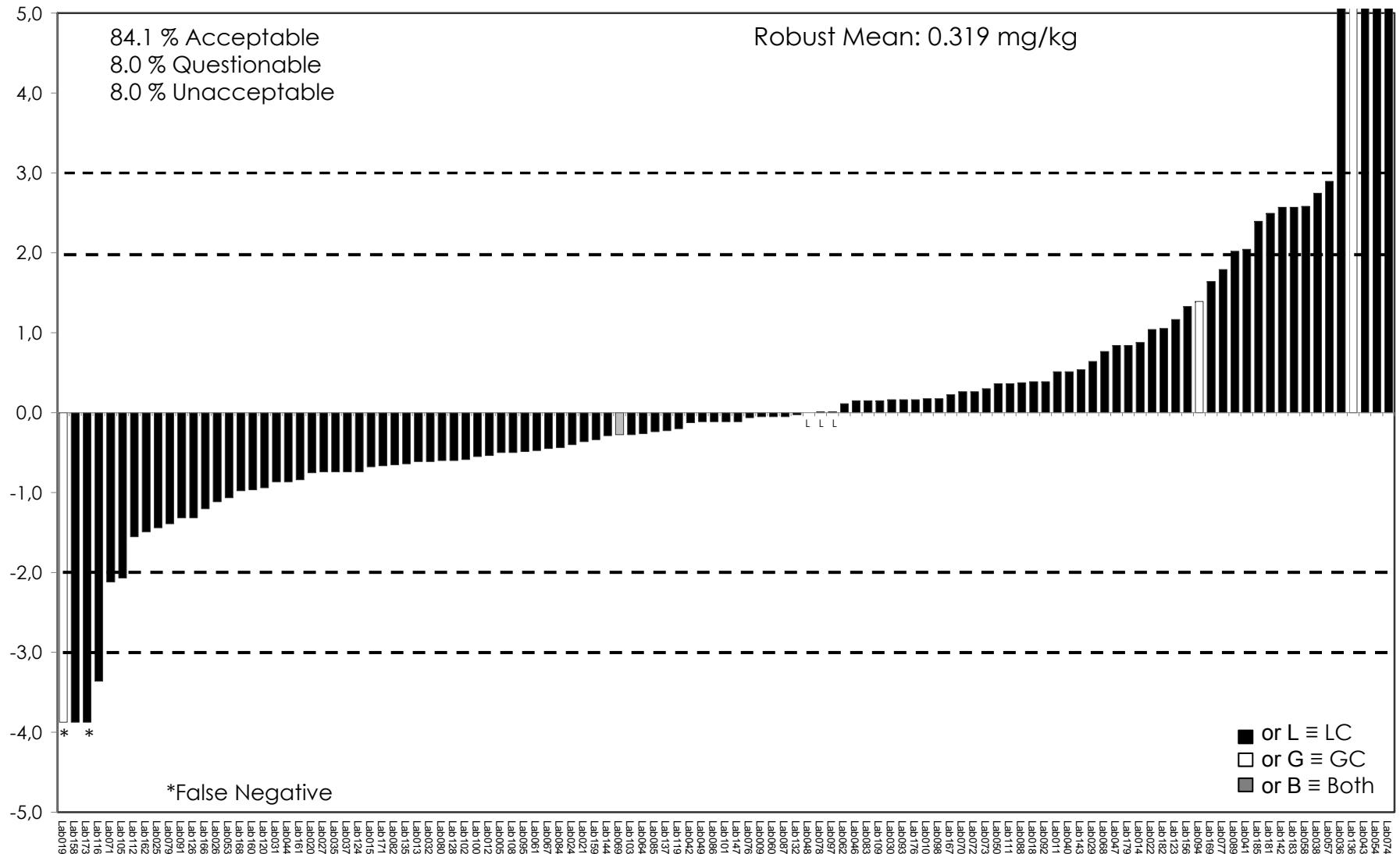
Diazinon



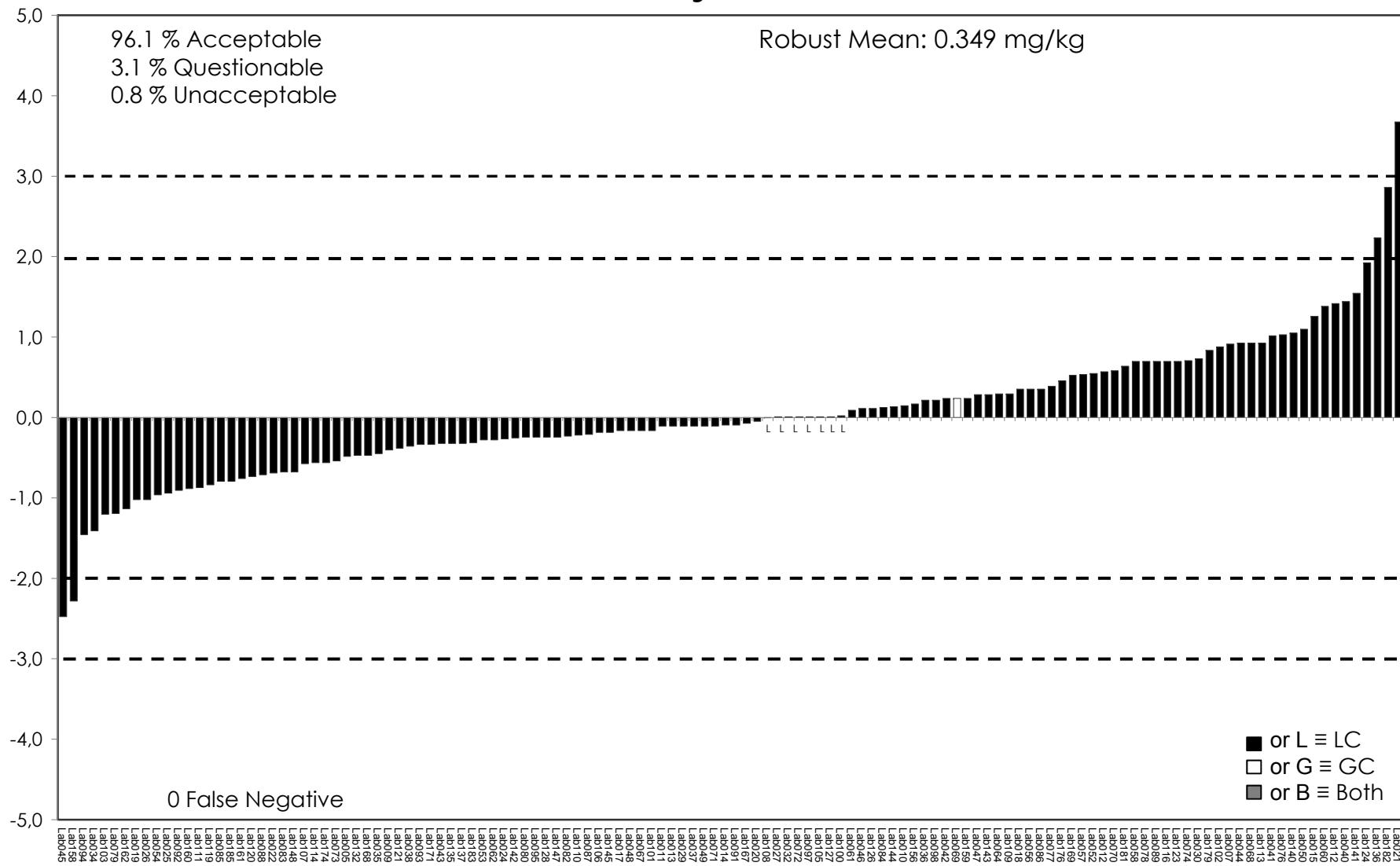
Difenoconazole



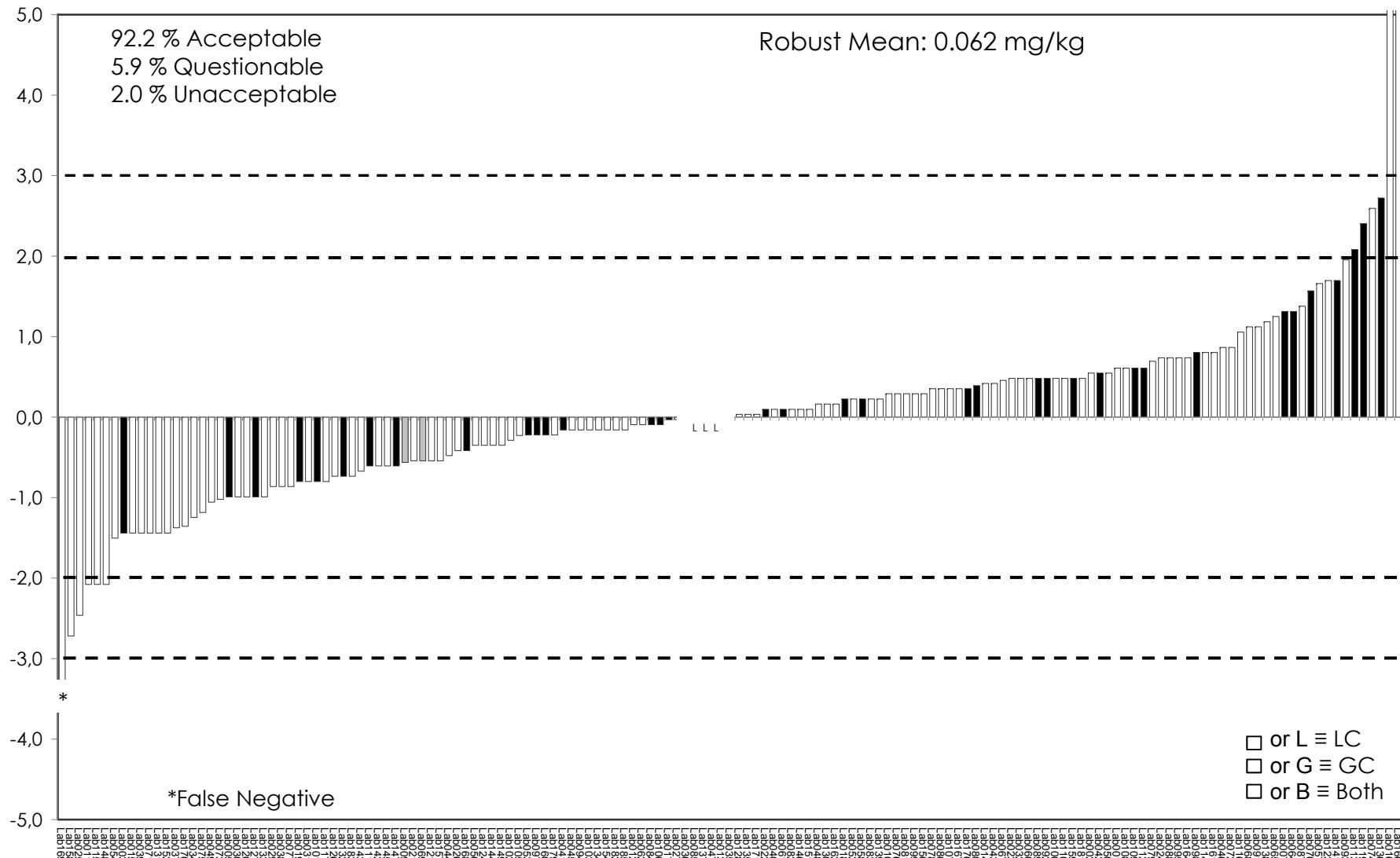
Diflubenzuron



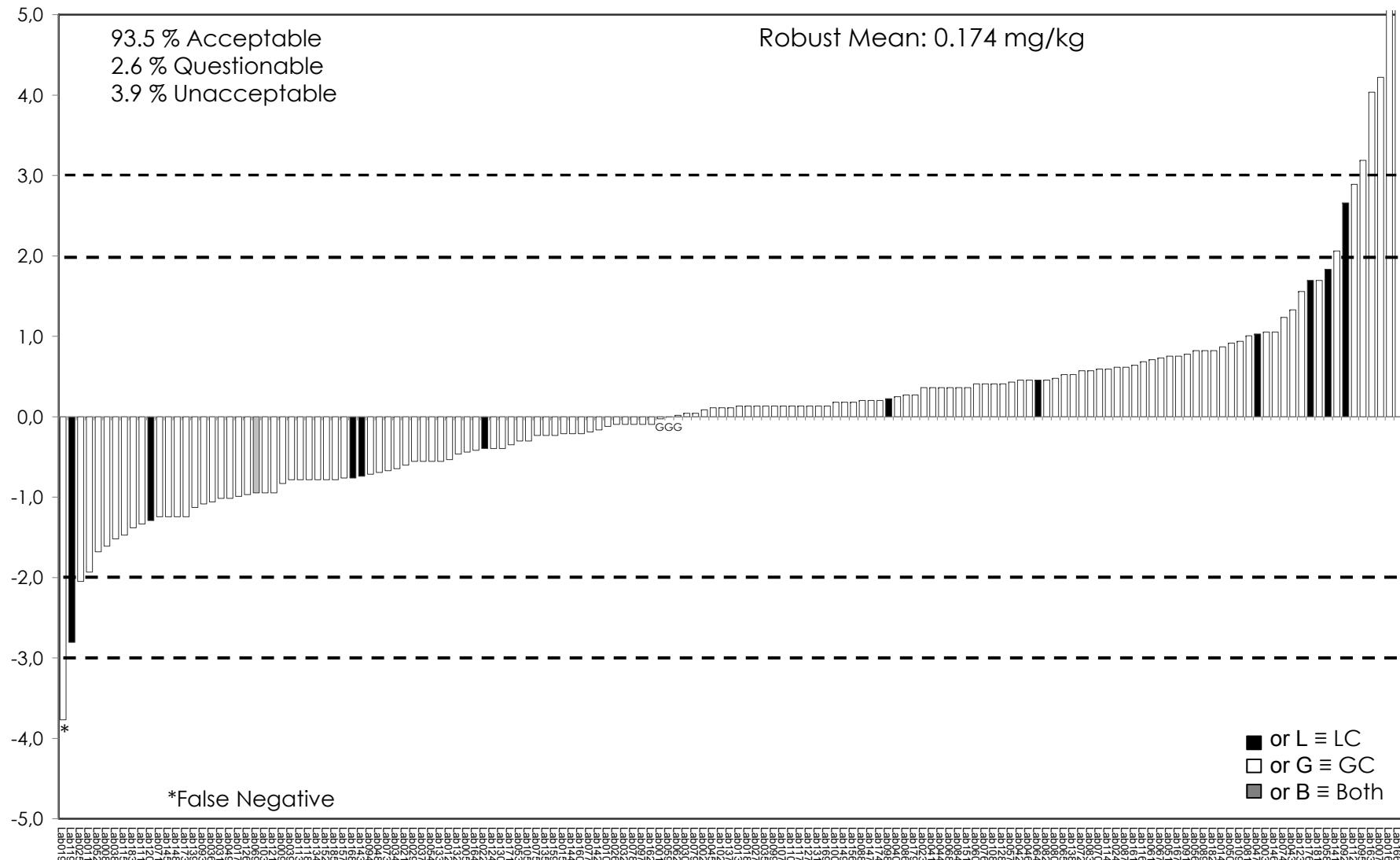
Methoxyfenozide



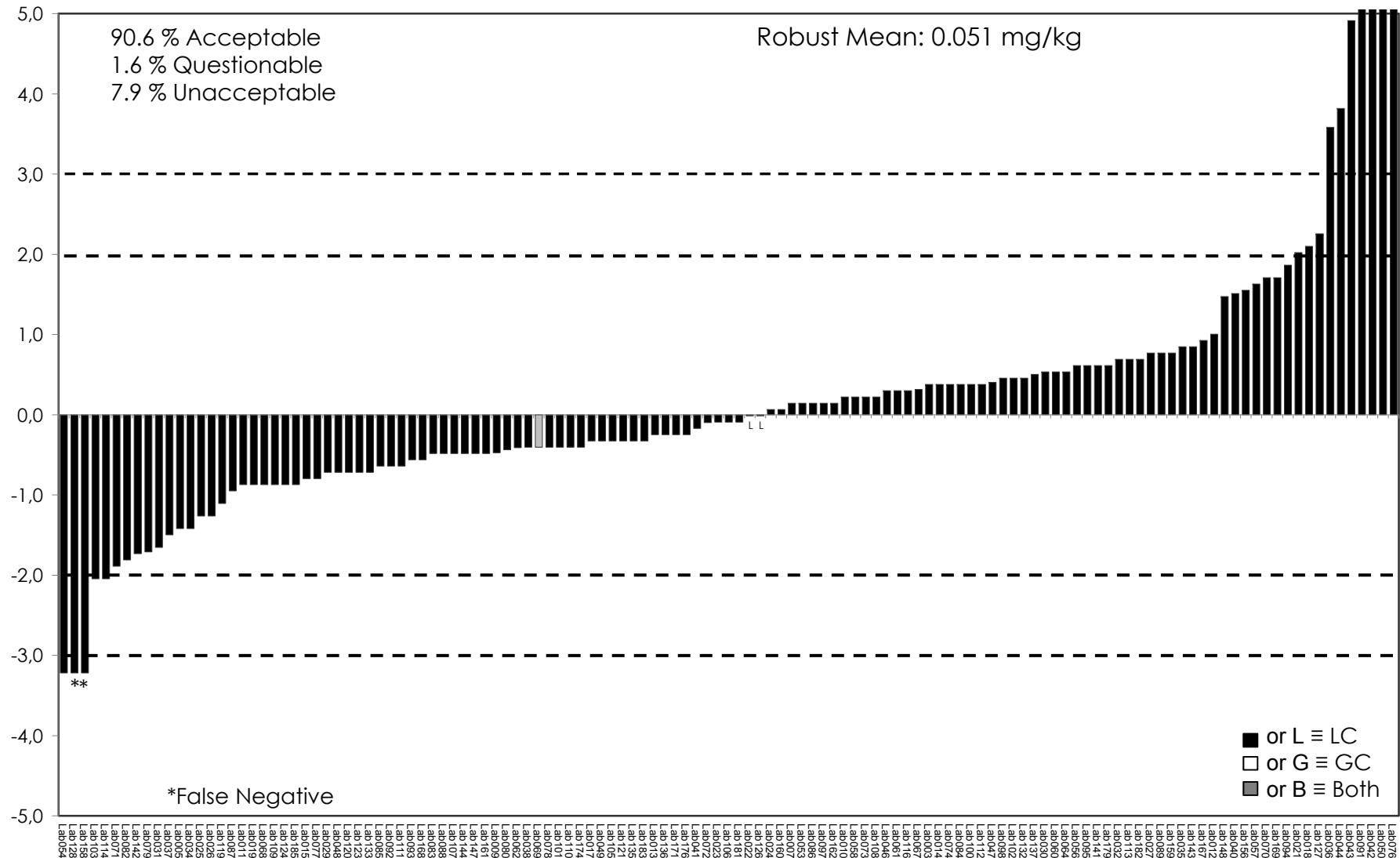
Pendimethalin



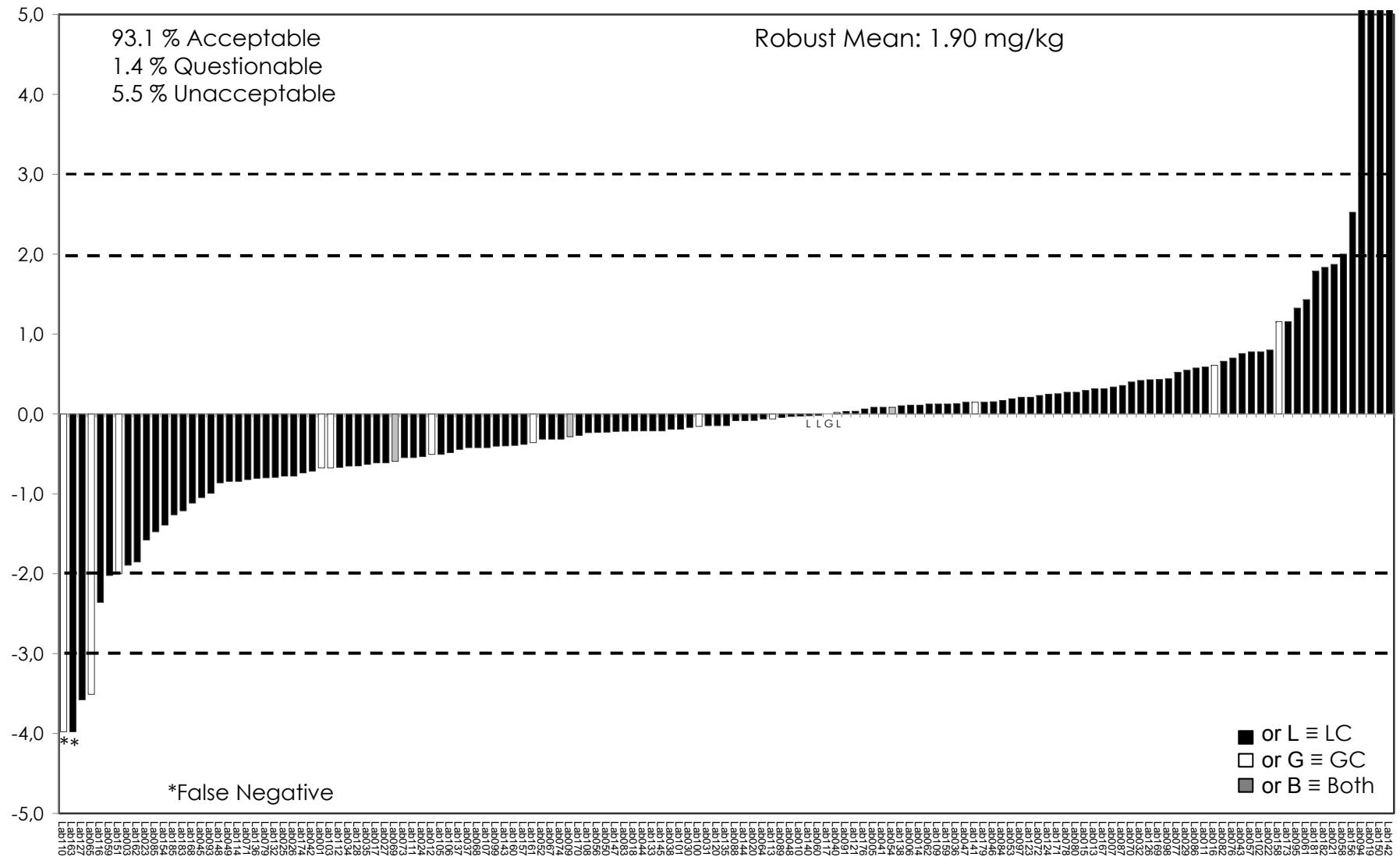
Permethrin



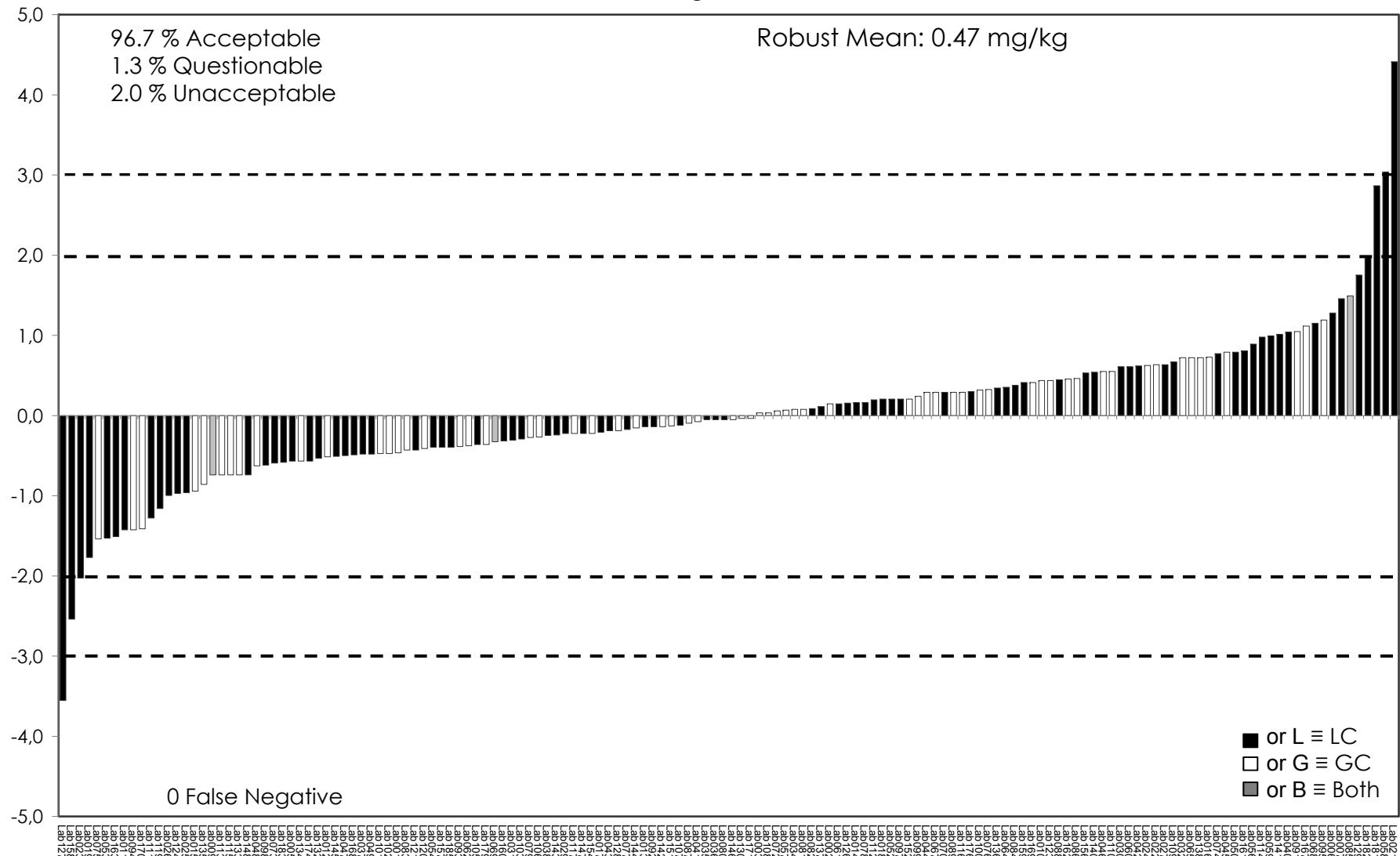
Spinosad



Thiabendazole

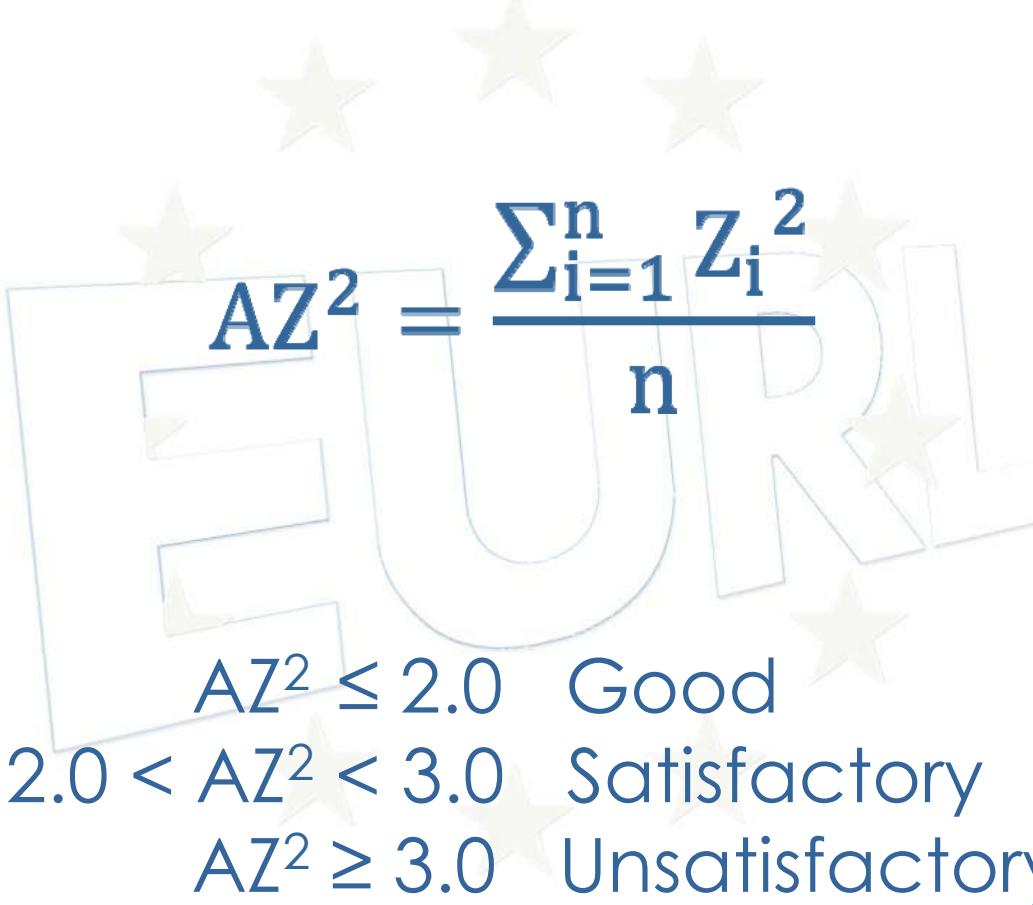


Trifloxystrobin



Combined z-Scores

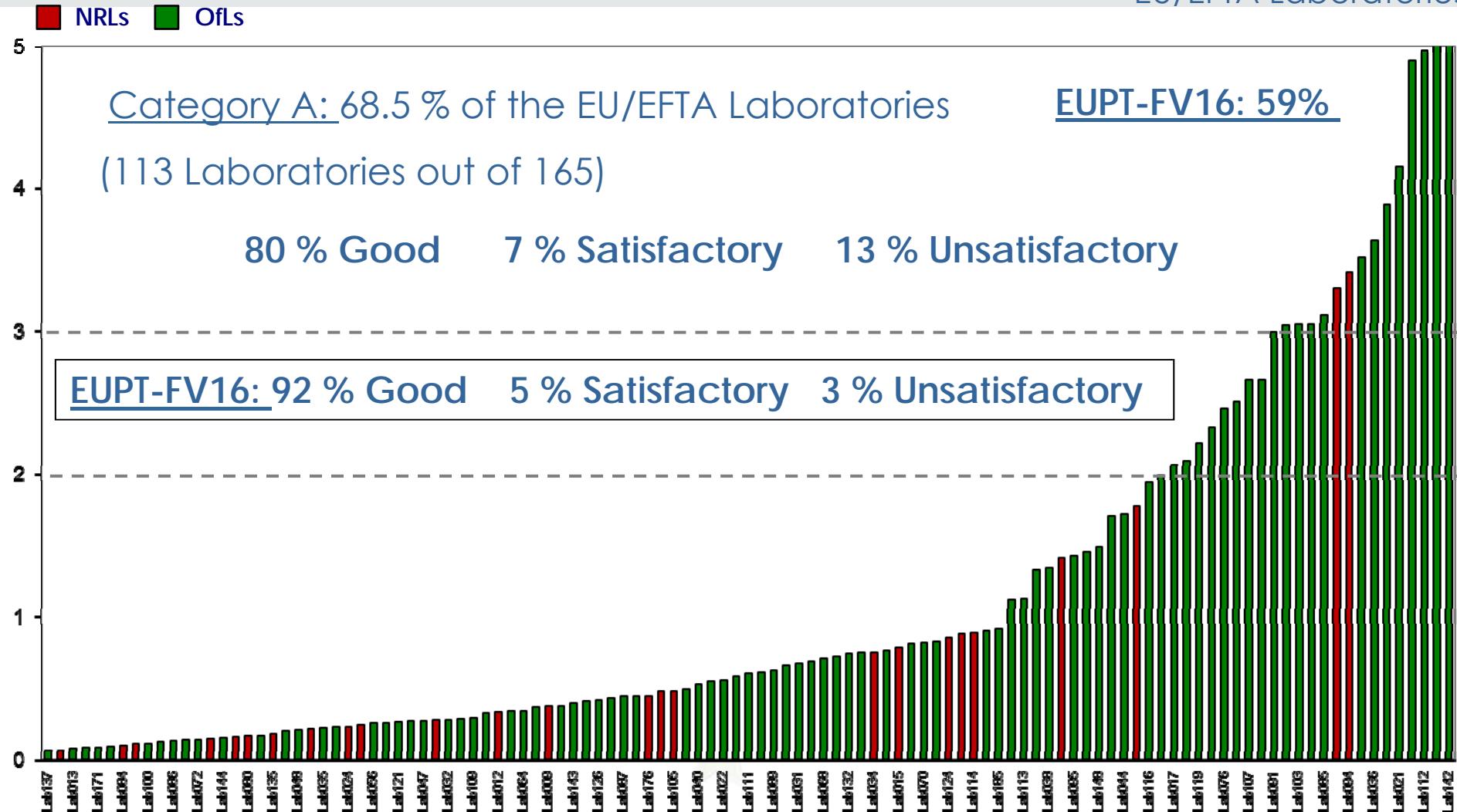
Average of Squared z-Scores


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

$AZ^2 \leq 2.0$ Good

$2.0 < AZ^2 < 3.0$ Satisfactory

$AZ^2 \geq 3.0$ Unsatisfactory



False Positives



6 different laboratories from EU/EFTA countries reported 6 pesticides as false positives

False Positives

Laboratory Code	Pesticide	Concentration (mg/kg)	Determination Technique	RL (mg/Kg)	MRRL (mg/Kg)
Lab027	Bromopropylate	0.014	GC-MS/MS	0.01	0.01
Lab098	Bromopropylate	0.021	GC-MS	0.01	0.01
Lab051	Bromopropylate	0.039	GC-MS	0.01	0.01
Lab173	Carbaryl	0.020	GC-MS/MS	0.01	0.01
Lab158	Fenpropathrin	0.020	GC-MS	0.01	0.01
Lab164	Kresoxim-methyl	0.015	GC-MS/MS	0.01	0.01
Lab173	Orthophenylphenol	2.95	HPLC-UV	0.1	0.01
Lab173	Tetradifon	0.014	GC-MS/MS	0.01	0.01

False Positives

GC-MS or GC-MS/MS

Bromopropylate

Carbaryl

Fenpropathrin

Kresoxim-methyl

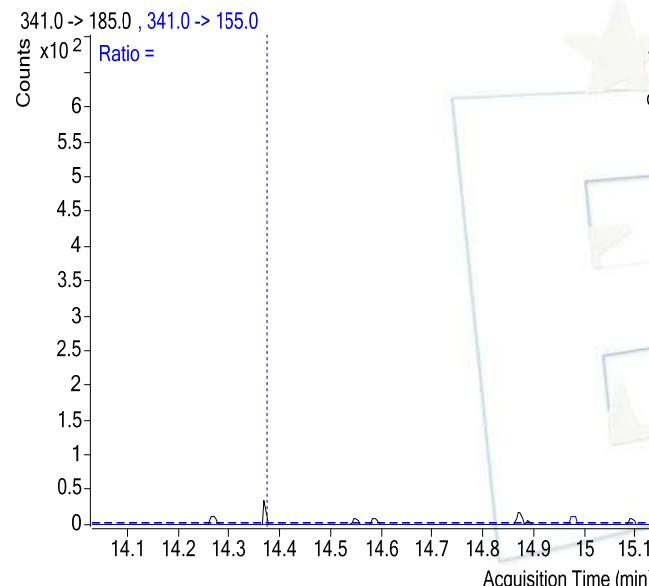
Tetradifon

HPLC-UV

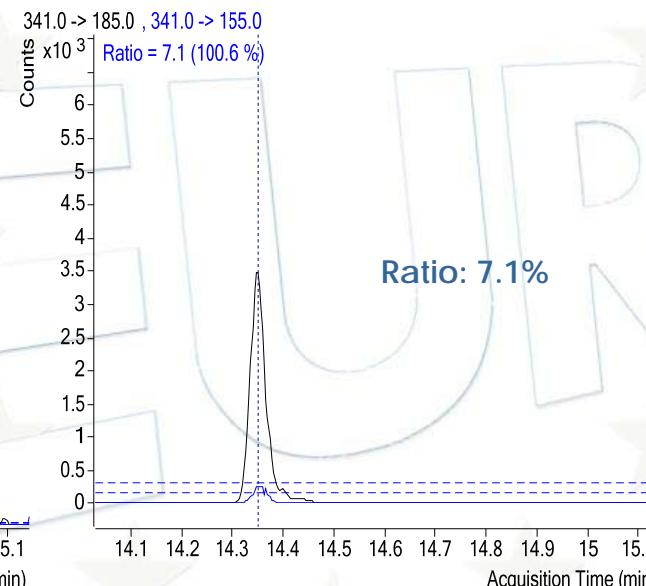
Orthophenylphenol

Bromopropylate in FV17

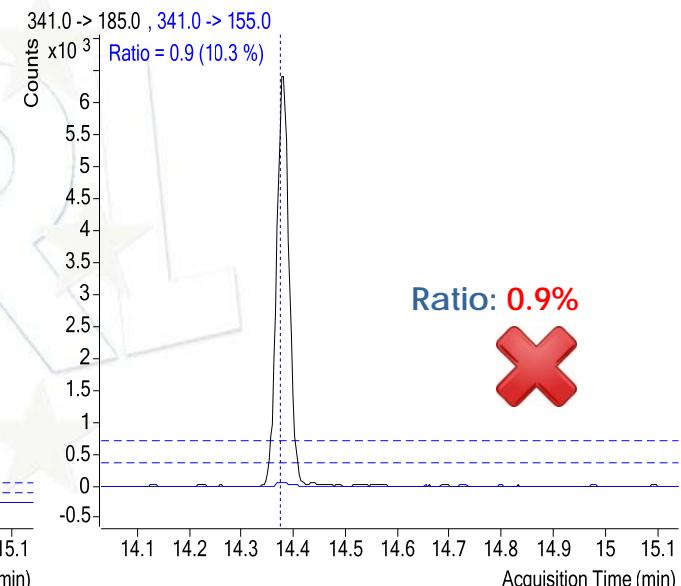
EUPT-FV17 Blank



10 µg/kg Std in Broccoli

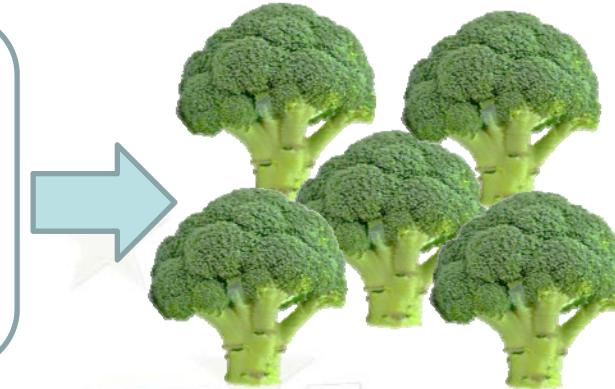


EUPT-FV17 Sample



MRM1: 341 > 185
 MRM2: 341 > 155

Bupirimate Carbendazim Diazinon
Difenconazole Diflubenzuron
Methoxyfenozide Pendimetalin
Permethrin Spinosad
Thiabendazole Trifloxystrobin



Cyprodinil

Ethirimol

Fludioxonil

Concentrations below MRRL (0.01 mg/kg)

Overview of the EUPTs-FV

Proficiency Tests - History

1995-2004

- 5 PTs on MRM in FV



Proficiency Tests - History

ISO/IEC 17043



Participant countries-Other countries (18)



EUPT-FV1 to EUPT-FV17 in numbers

EUPT Nº	Matrices	Nº of Participants	Nº of Possible Pesticides	Nº of pesticides evaluated in test item
1	Pepper	88	33	6
2	Apple	85	41	6
3	Cucumber	116	48	14
4	Orange	117	57	14
5	Lettuce	127	57	15
6	Tomato	130	57	13
7	Grape	128	65	16
8	Aubergine	129	68	16
9	Strawberry	137	82	19
10	Carrot	132	113	18
11	Cauliflower	151	128	21
12	Leek	153	144	17
13	Mandarin	154	144	19
14	Pear	167	175	18
15	Potato	175	175	18
16	Pepper	183	175	22
17	Broccoli	185	183	11

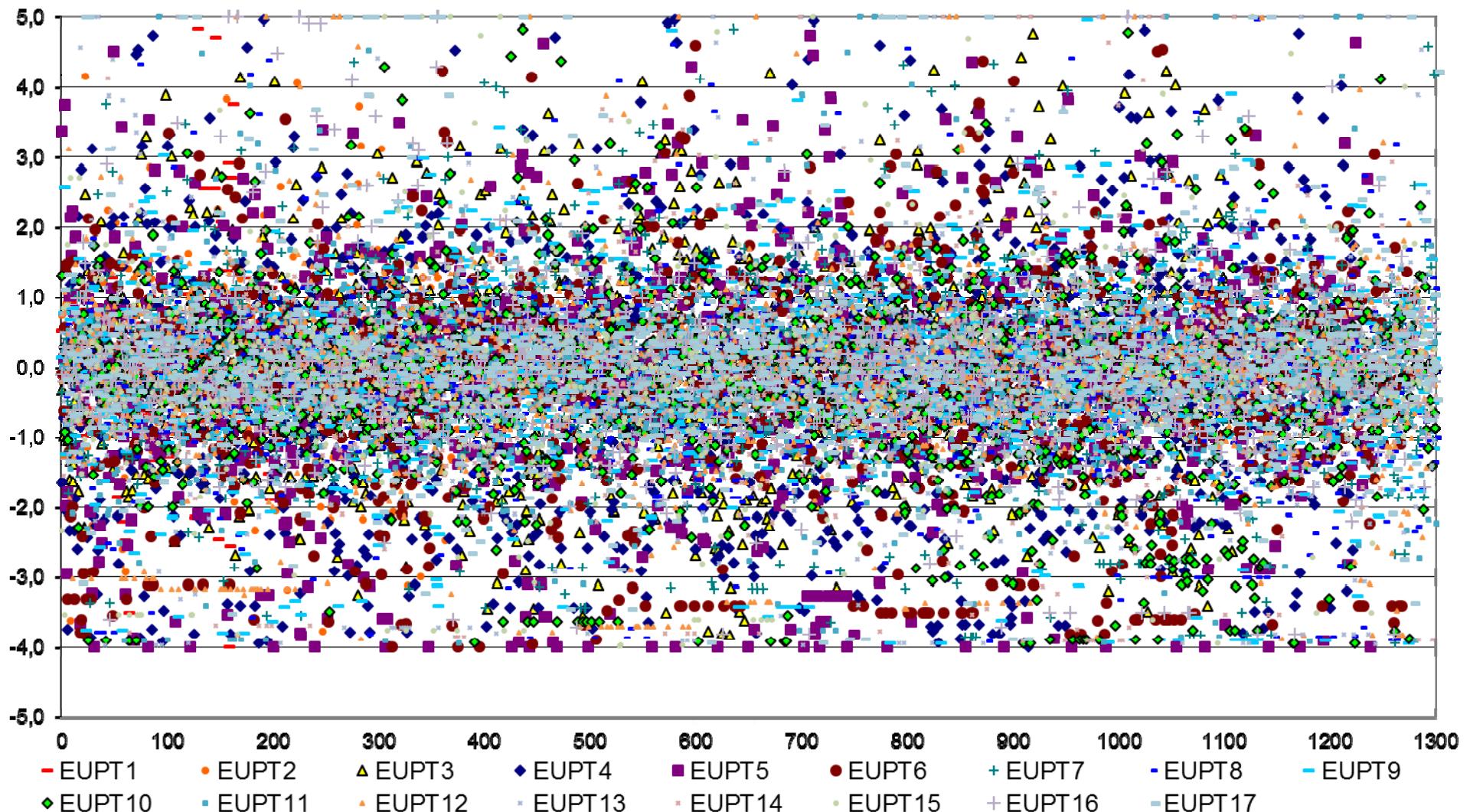


Pesticides Used to Treat the Sample in last ten EUPT-FVs

Acephate	Difenoconazole	Kresoxim-methyl	Pirimicarb
Acetamiprid	Diflubenzuron	Lambda-Cyhalothrin	Pirimphos-methyl
Acrinathrin	Dimethoate	Linuron	Prochloraz
Aldicarb(sum)	Diphenilamine	Malathion	Procydimone
Amitraz (DMPF&DMF)	Dithiocarbamates(CS2)	Mecarbam	Propoxur
Azinphos-methyl	Endosulfan	Metalaxyl	Propyzamide
Azoxystrobin	EPN	Metamidophos	Prothiofos
Bifenthrin	Fenamiphos	Methidathion	Pyraclostrobin
Boscalid	Fenamiphos sulfone	Methiocarb sum	Pyridaben
Bromopropylate	Fenamiphos sulfoxide	Methiocarb	Pyrimethanil
Bupirimate	Ethion	Methomyl	Pyriproxifen
Buprofezin	Fenhexamid	Methoxyfenozide	Quinoxyfen
Cadusafos	Fenitrothion	Methyl-Tiophanate	Quintozene
Captan	Fenpropothrin	Mevinphos	Spinosad
Carbaryl	Fludioxinil	Monocrotophos	Spirodiclofen
Carbendazim	Flufenoxuron	Myclobutanil	Tebuconazole
Carbofuran sum	Fluopicolide	Omethoate	Tetraconazole
Chlorpropham	Flutolanil	Ortophenilphenol	Thiabendazole
Chlorpyrifos	Folpet	Oxamyl	Thiacloprid
Chlorpyrifos-methyl	Fosthiazate	Oxydemeton-methyl	Tolclofos-methyl
Chlothalonil	Hexythiazox	Parathion	Tolyfluanid
Cypermethrin	Imazalil	Penconazole	Triadimenol
Cyprodinil	Imidacloprid	Pencycuron	Triazophos
Delthamethrin	Indoxacarb	Pendimethalin	Trifloxystrobin
Diazinon	Iprodione	Permethrin	Triflumuron
Dichlofuanid	Iprovalicarb	Phosalone	Vinclozolin
Dicofol	Isofenphos-methyl	Phosmet	

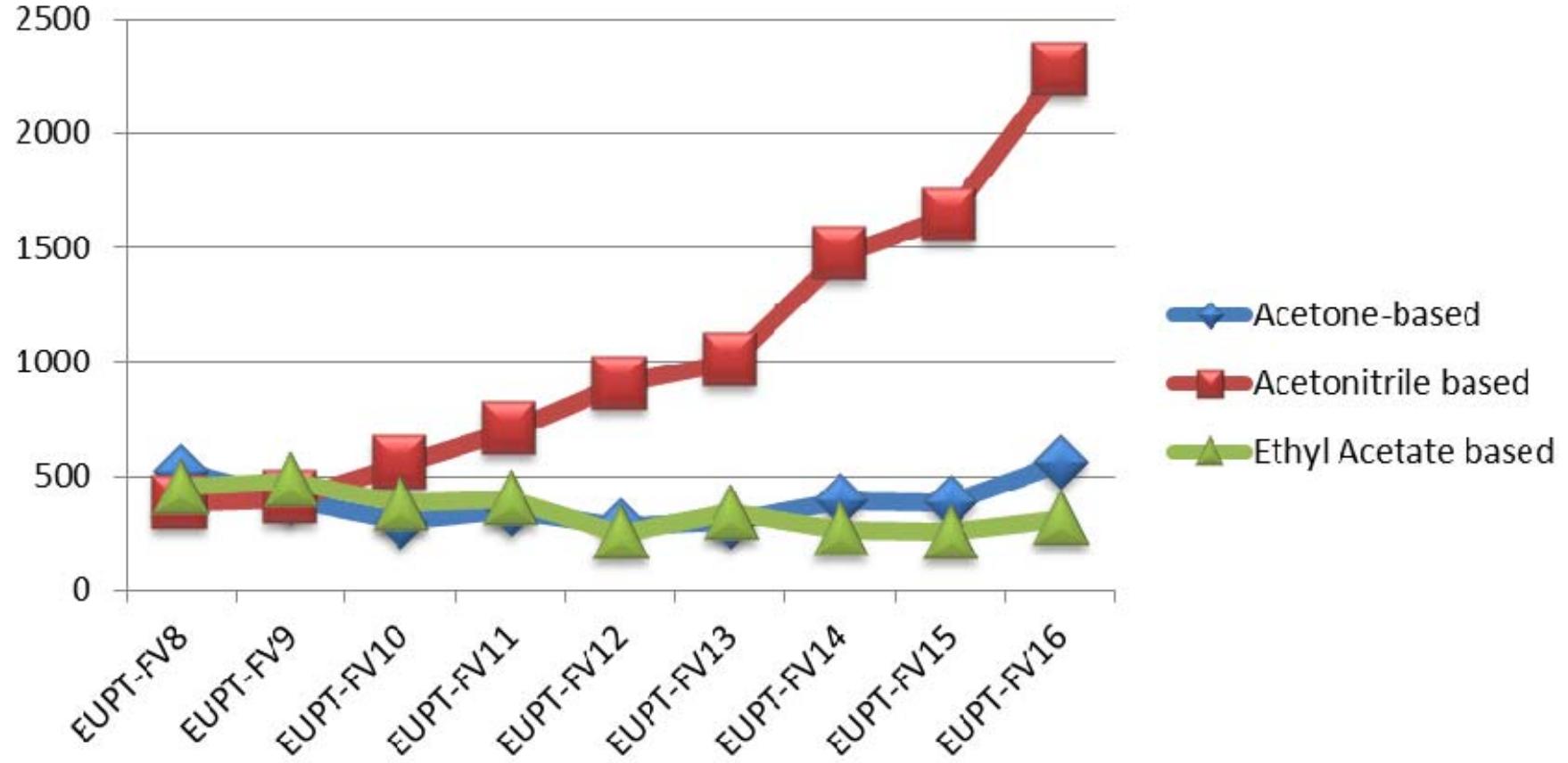
Summary of Results

17 EUPTs z-Score Results (28831)



Extraction methods

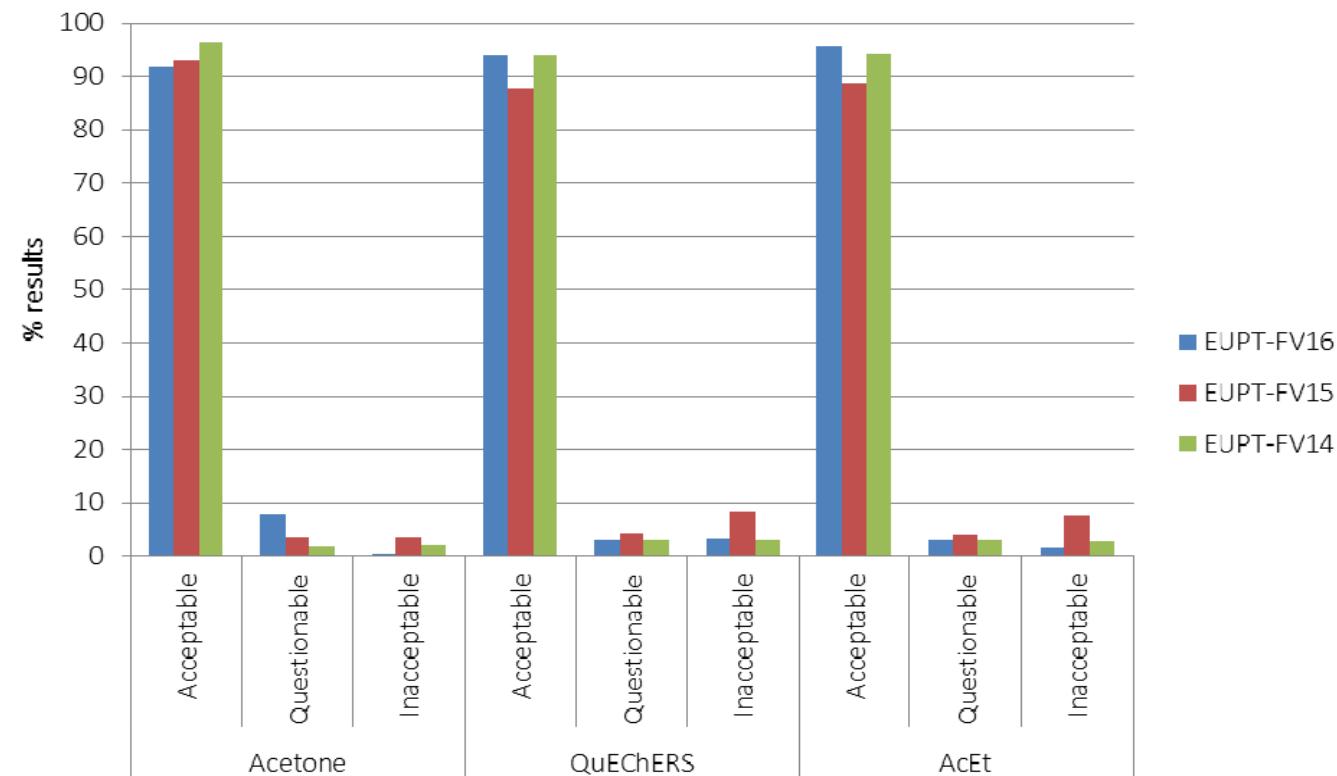
Number of results reported by extraction method



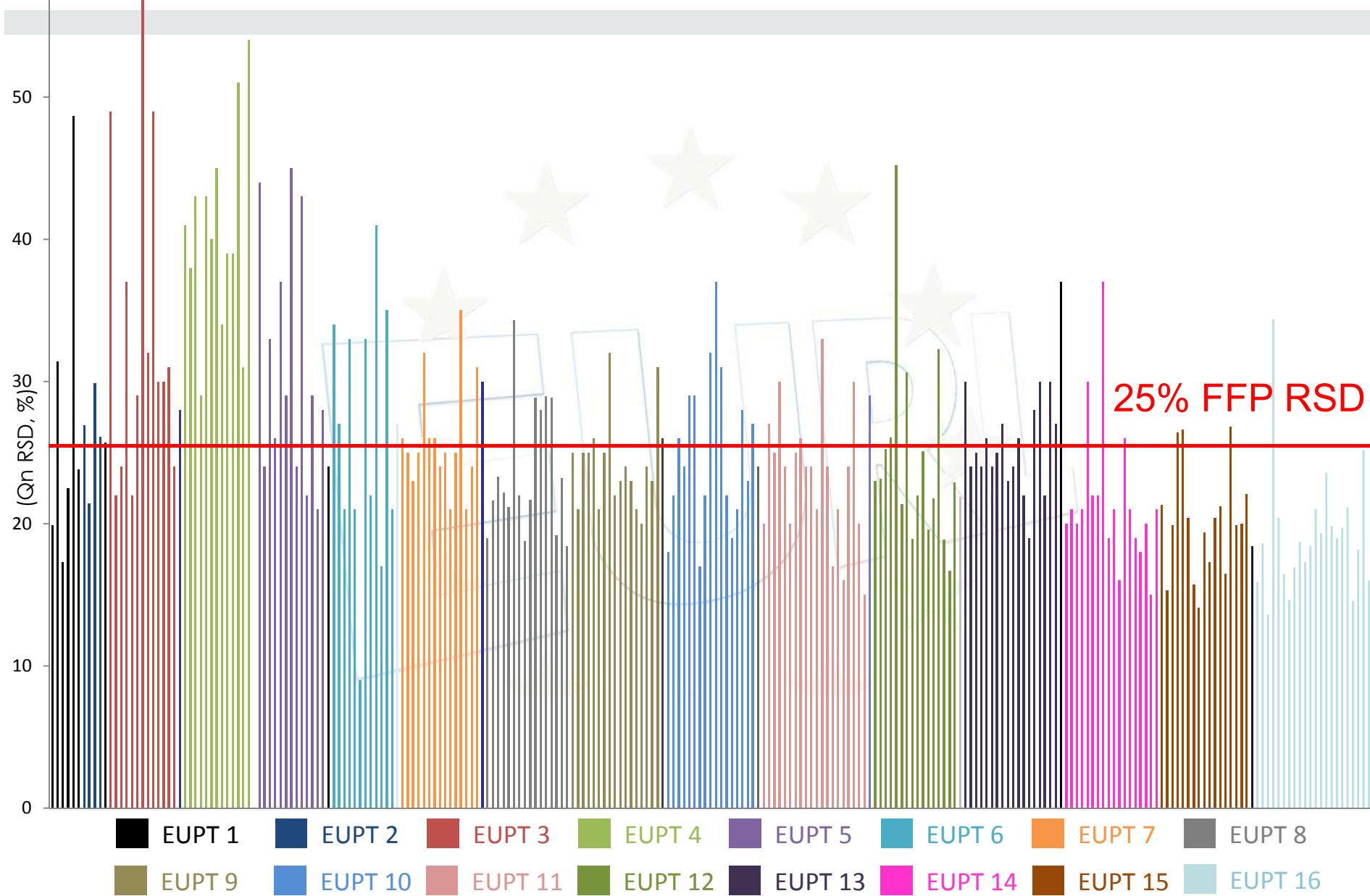
Extraction methods

Classification of z-scores by extraction method

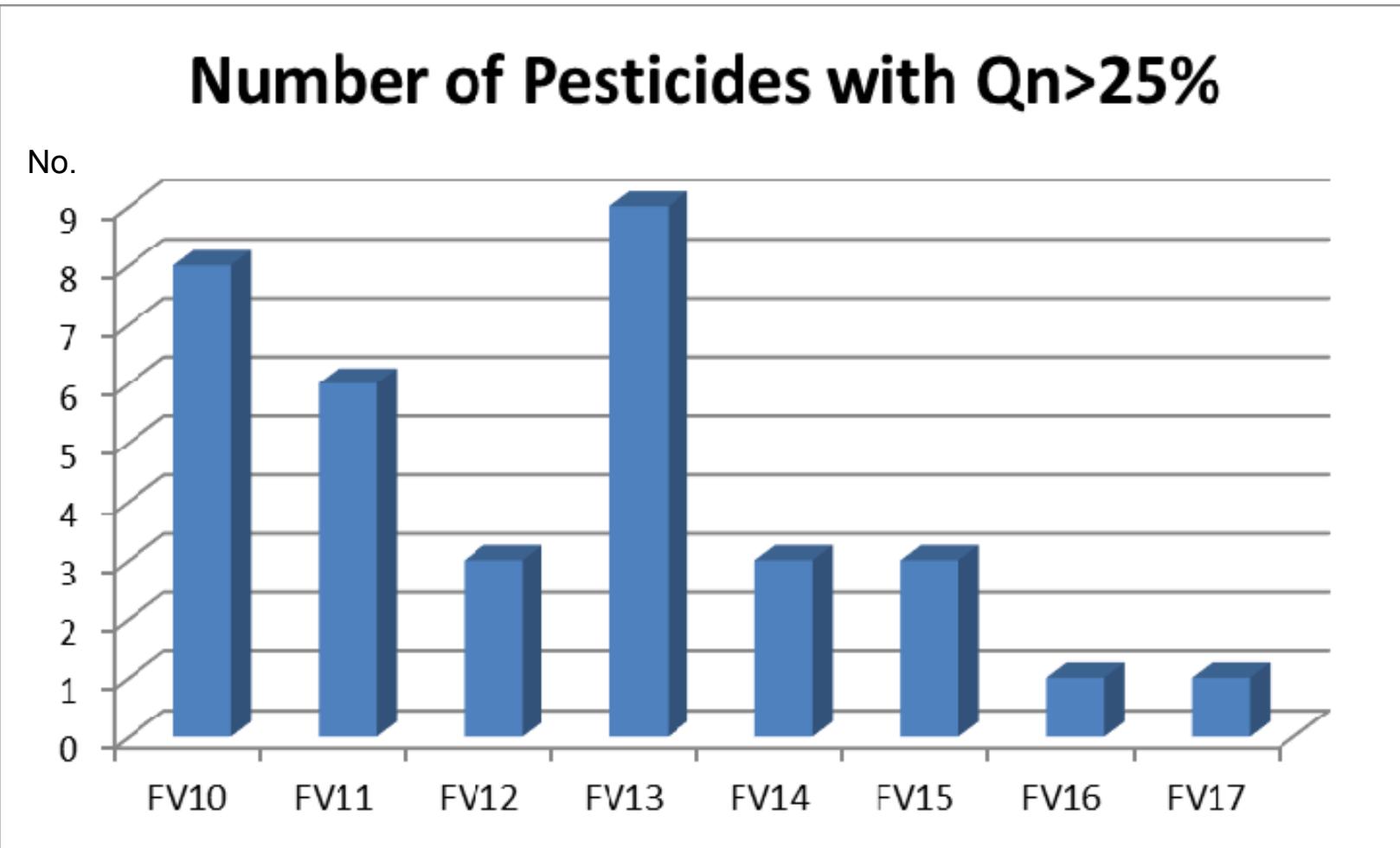
	Acetone			QuEChERS			AcEt		
	Acceptable	Questionable	Inacceptable	Acceptable	Questionable	Inacceptable	Acceptable	Questionable	Inacceptable
EUPT-FV16	91,7	7,7	0,6	93,9	2,9	3,2	95,5	2,9	1,6
EUPT-FV15	93,0	3,4	3,6	87,7	4,2	8,2	88,6	3,9	7,5
EUPT-FV14	96,2	1,8	2	93,9	3,1	3	94,3	3	2,7



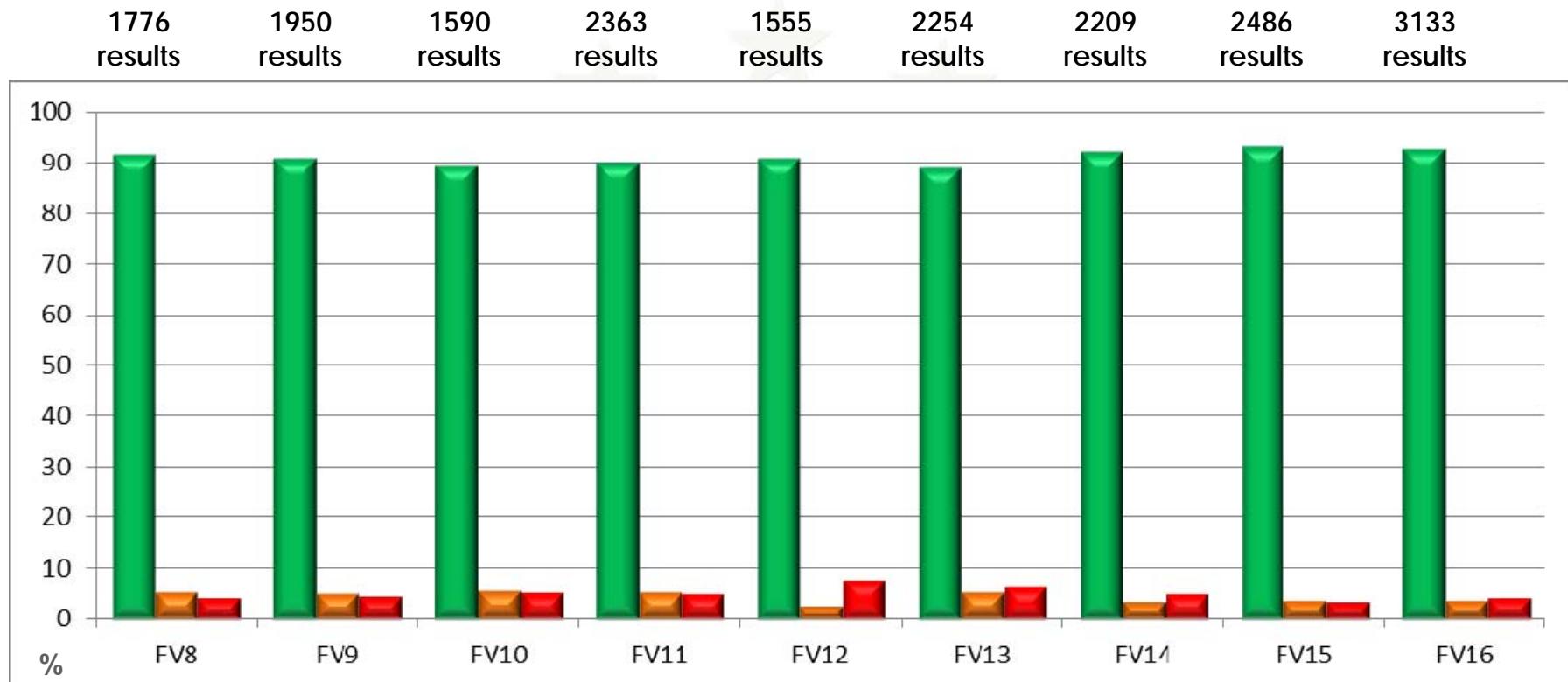
Dispersion of Results (RSD, %)



Dispersion of Results (RSD, %)



Classification of z-scores

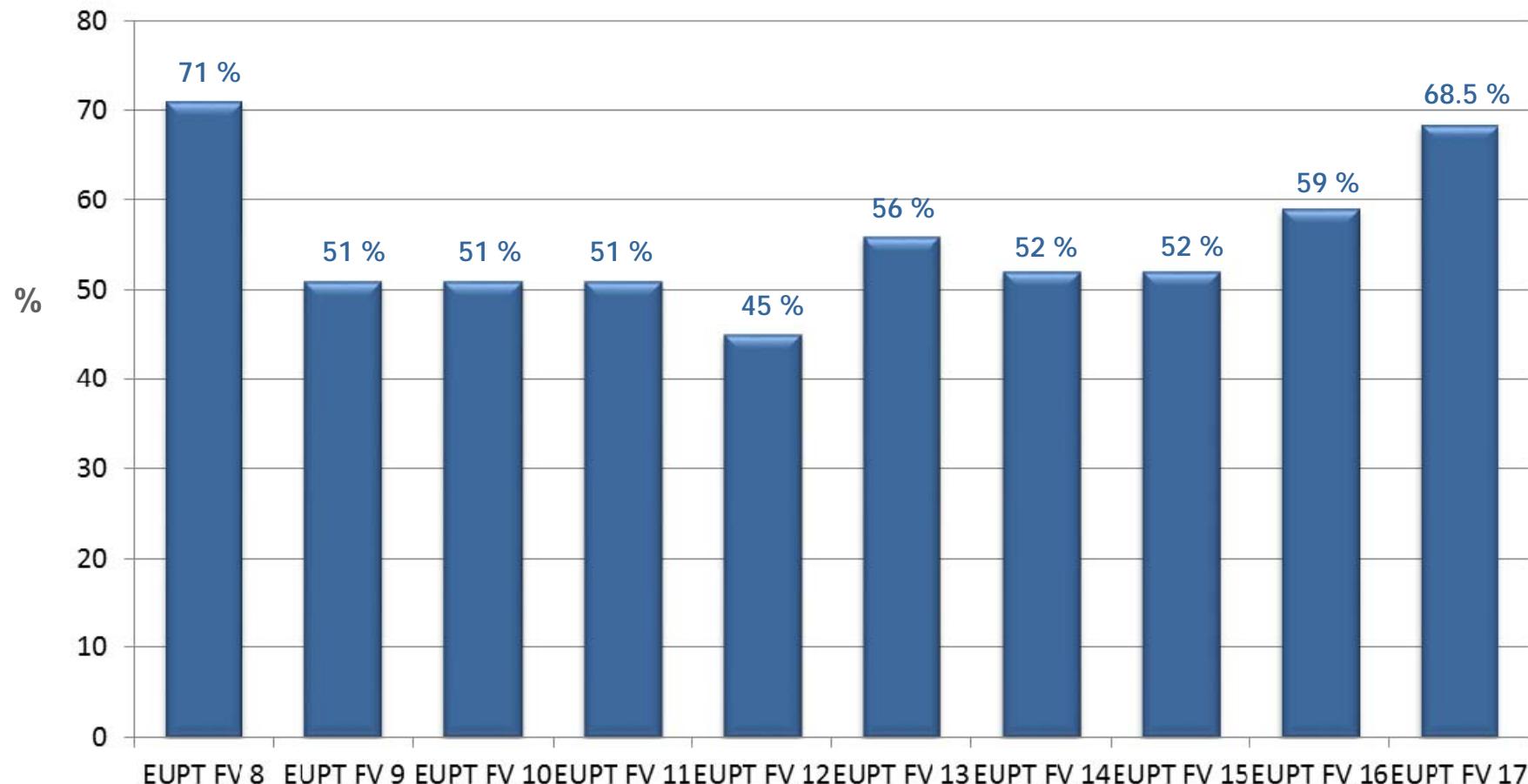


Acceptable

Questionable

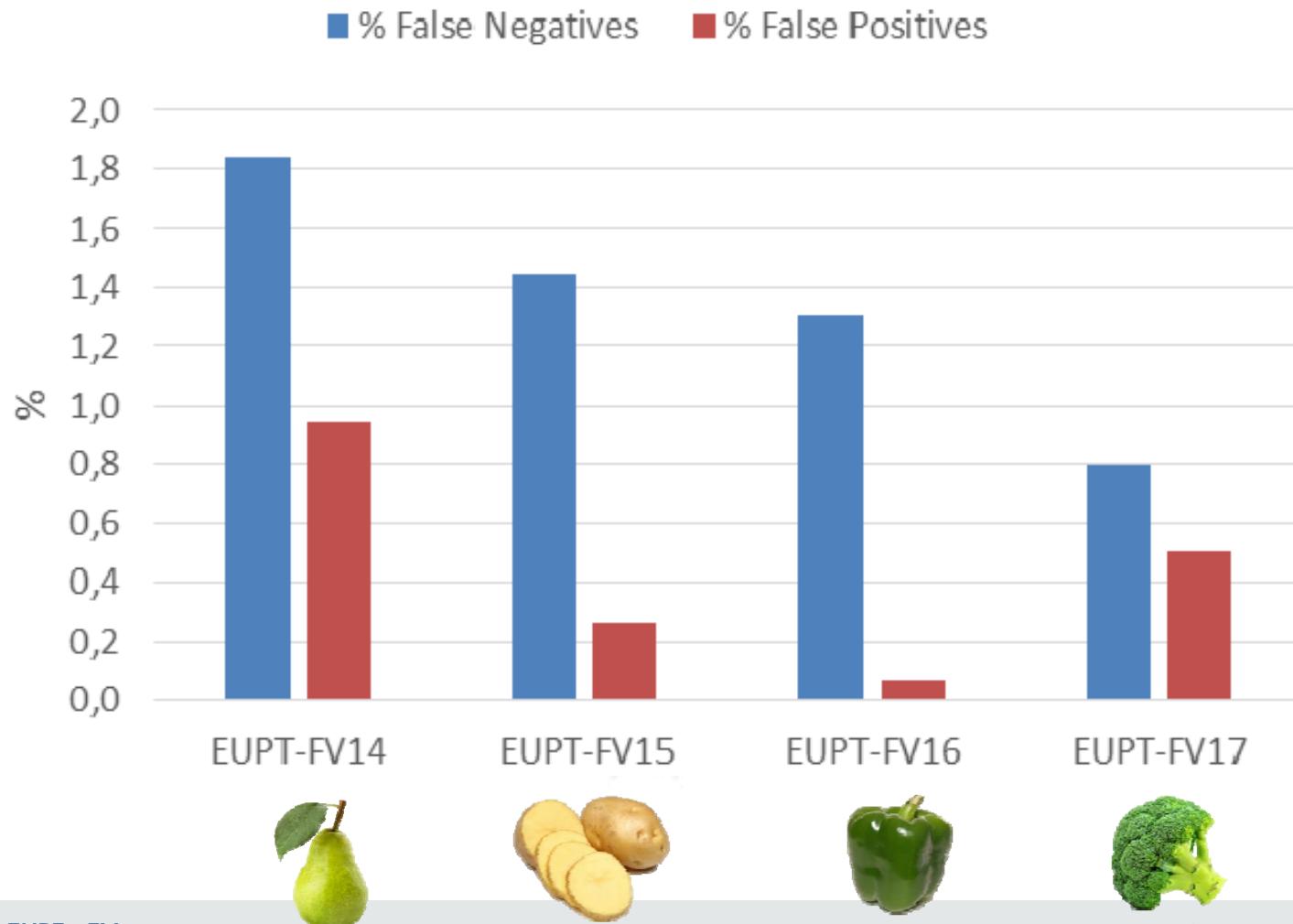
Unacceptable

Laboratories in Category A



False Negatives and Positives

Percetange of False Positives and Negatives



**Thank You
for Your Attention**



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