4th Joint Workshop of the EUROPEAN UNION REFERENCE LABORATORIES

Almería (SPAIN) 23rd-25th OCT 2013

EUROPEAN COMMISSION
PROFICIENCY TEST
FOR PESTICIDE RESIDUES IN FRUITS
AND VEGETABLES 15

EUPT-FV-15

CARMEN FERRER

European Commission
EURL
EUROPEAN UNION REFERENCE LABORATORIES

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EUPT-FV-15
European Proficiency Test FV-15

Participation

EUPT-FV-15
European Proficiency Test FV-15

Country	No. of Labs	Country	No. of Labs	Country	No. of Labs
Austria	3 (-1)	Greece	10	Portugal	3
Belgium	8 (+4)	Hungary	4	Romania	3
Brazil	1 (-1)	Iceland	1	Saudi Arabia	1 New
Bulgaria	2 (+1)	India	1	Serbia	1
China	2 New	Ireland	1	Slovakia	2
Cyprus	1	Israel	1	Slovenia	3
Croatia	3	Italy	24	Spain	28 (+3)
Czech Republic	3 (+1)	Latvia	1	Sweden	2
Denmark	2	Lithuania	1	Switzerland	3 (-1)
Estonia	2	Luxembourg	2 (+1)	The Netherlands	2
Finland	2	Malta	2 (-1)	Turkey	1
France	10 (+1)	Morocco	1 New	United Kingdom	4
		Norway	1	Uruguay	1
Germany	25 (+2)	Poland	11 (+2)	Total No. of Labs = 175 Total No. of non EU/EFTA Labs = 13 Total No. of Countries = 40	

Participation

Total No. of Labs = 175	Total No. of Countries = 40
EU/EFTA Labs = 162	EU/EFTA countries = 30
Other countries Labs = 13	Other countries = 10

(27 EU + 3 EFTA + 1 acceding country* + 2 Candidate countries + 7 other countries)

*Although it is now an EU member state, Croatia was acceding country when the exercise took place

EUPT-FV-15
European Proficiency Test FV-15

175 pesticides

3-hydroxy-carbofuran
Acephate
Acetamiprid
Acrinathrin
Aldicarb
Aldicarb Sulfone
Aldicarb Sulfoxide
Amitraz
Azinphos-methyl
Azoxystrobin
Benfuracarb
Bifenthrin
Bitertanol
Boscalid
Bromopropylate
Bromuconazole
Bupirimate
Buprofezin
Cadusafos*
Captan
Carbaryl
Carbendazim
Carbofuran
Carbosulfan
Chlorfenapyr
Chlorfenvinphos
Chlorobenzilate*
Chlorothalonil
Chlorpropham
Chlorpyrifos
Chlorpyrifos-methyl
Clofentezine
Clothianidin
Cyfluthrin
Cypermethrin
Cyproconazole
Cyprodinil
Deltamethrin
Demeton-S-methylsulfone
Desmethyl-pirimicarb
Diazinon
Dichlofluanid
Dichlorvos
Dicloran
Dicofol
Difenoconazole
Diflubenzuron
Dimethoate
Dimethomorph
DMST
Diphenylamine
DMF
DMPF
Endosulfan alpha
Endosulfan beta
Endosulfan sulfate
EPN
Epoxiconazole
Ethion
Ethoprophos
Etofenprox
Fenamiphos
Fenamiphos sulfone
Fenamiphos sulfoxide
Fenarimol
Fenazaquin
Fenbuconazole
Fenhexamid
Fenitrothion
Fenoxycarb
Fenpropathrin
Fenpropimorph
Fenthion
Fenthion oxon
Fenthion oxon sulfone
Fenthion oxon sulfoxide
Fenthion sulfone
Fenthion sulfoxide
Fipronil
Fludioxonil
Flufenoxuron
Fluopicolide*
Fluquinconazole
Flusilazole
Flutolanil*
Flutriafol
Folpet
Fosthiazate
Hexaconazole
Hexythiazox
Imazalil
Imidacloprid
Indoxacarb
Iprodione
Iprovalicarb
Isofenphos-methyl
Kresoxim-methyl
Lambda-Cyhalothrin
Linuron
Lufenuron
Malaoxon
Malathion
Mepanipyrim
Metaflumizone*
Metalaxyl and metalaxyl-M
Metconazole
Methamidophos
Methidathion
Methiocarb
Methiocarb sulfone
Methiocarb sulfoxide
Methomyl
Methoxyfenozide
Monocrotophos
Myclobutanil
Omethoate
Orthophenylphenol
Oxadixyl
Oxamyl
Oxydemeton-methyl
Paclobutrazole
Paraoxon-methyl
Parathion-ethyl
Parathion-methyl
Penconazole
Pencycuron
Pendimethalin
Phenthoate
Phosalone
Phosmet
Phosmet oxon
Phoxim
Pirimicarb
Pirimiphos-methyl
Prochloraz
Procymidone
Profenofos
Propargite
Propiconazole
Propyzamide
Prothioconazole
Prothiofos
Pyraclostrobin
Pyridaben
Pyrimethanil
Pyriproxyfen
Quinoxyfen
Spinosad
Spirodiclofen
Spiroxamine
Tau-Fluvalinate
Tebuconazole
Tebufenozide
Tebufenpyrad
Teflubenzuron
Tefluthrin
Tetraconazole
Tetradifon
Thiabendazole
Thiacloprid
Thiamethoxam
Thiodicarb
Thiophanate-me
Tolclofos-methyl
Tolylfluanid
Triadimefon
Triadimenol
Triazophos
Trichlorfon
Trifloxystrobin
Triflumuron
Trifluralin
Triticonazole
Vinclozolin
Zoxamide

*Not in the coordinated multiannual control programme

Pesticides used for the treatment	
Acephate	Linuron
Azoxystrobin	Methiocarb
Chlorpropham	Pencycuron
Chlorothalonil	Prochloraz
Cypermethrin	Procymidone
Diazinon	Spirodiclofen
Fluopicolide*	Thiabendazole
Flutolanil*	Thiacloprid
Fosthiazate	Total: 18
Iprovalicarb	

**** Not in the* coordinated multiannual control programme**

New in the target list

*** COMMISSION IMPLEMENTING REGULATION (EU) No 788/2012 of 31 August 2012 concerning a coordinated multiannual control programme of the Union for 2013, 2014 and 2015 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 .**

CALENDAR

ACTIVITY	DATE
- Publishing the Target Pesticide List, Calendar on the Web page	22nd October 2012
- Receiving Application Form from invited laboratories.	3rd Dec 2012 - 7th Jan 2013
- Specific Protocol published on the Web site	7th Jan 2013 at the latest
- Filling in the Laboratory Scope from the Participants: Form 0	8th-18th January 2013
- Sample distribution.	**21st January 2013**
- Deadline for receiving sample acceptance: Form 1	25th January 2013
- Deadline for receiving results: Form 2, Form 3 and Form 4	**13th February 2013**
- Filling in Form 5	20th-27th February 2013
- Preliminary Report: provisional results, medians and z-scores.	April 2013
- Final Report to the Laboratories	December 2013

WEB PAGE: Forms

Main Page EUPT-FV 15

Link to Result - Submission:

0. Laboratory scope

Specify which pesticides you analysed for.

Deadline 18th Jan 2013

1. Test Material Receipt

Acknowledge receipt of test material.

Deadline 25th Jan 2013

2. Detected pesticides

Specify which pesticides you have detected.

Deadline 13th Feb 2013

3. Results

Enter your analitycal results.

Deadline 13th Feb 2013

4. Methods

Describe the methods used for your analyses.

Deadline 13th Feb 2013

5. Additional Information Requested

Describe the methods used for your analyses

Deadline 27th Feb 2013

European Union Proficiency Test on Pesticide Residues in Fruits and Vegetables - EUPT-FV 15 2013

Welcome to the results submission pages.

To submit results for EUPT-FV-15 you have to enter your data into the 6 subpages 0-5. Each page contains instructions on how to enter the data and
each page must be saved separately.

First of all, fill in the laboratory scope form indicating the pesticides you analize 0.Laboratory scope from the Target Pesticide List click here to download it.

When you receive the sample, please enter subpage 1.Test Material Receipt

To report results start with: 2. Detected Pesticides. For the list you report in Form 0, indicate which ones you have detected. New validated pesticides may be marked as detected.

Continue with page: 3. Results. Here you can enter your results for the pesticides you have detected, concentrations and recoveries.

Next page: 4. Methods. Here you must enter information about the methods you have used. For each detected pesticide indicate details about the analytical procedure, e.g. sample weight, extraction solvents, GC- and HPLC-detectors,...

Finalize with page: 5. Additional Information Requested. This Form will be accessible, after the deadline for submitting results. Here you will be requested to enter information about the methods you have used for each one of the pesticides you have analysed for but you have not detected in the sample (these are the false negatives). The system will request you the pesticides that you need to fill in that were present in the sample. **No changes will be accepted on the concentration results.**

Remember to save any page separately before you leave it.

When you click "save" in the webpages the data will be stored, after the deadline all your data in the database will be downloaded by the organization to create the final report, you don't need to send us any document

You can enter into the different pages as many times as you wish until the deadline. You can e.g. enter all data for the GC pesticides one day (on page 1 to 4) and the LC results another day. Just remember to enter data in the right order from page 0 to 5. If you need to correct the data, this must be done before the deadline.

Click here to get an excell with all your inputs.

Contact Persons:

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EUPT-FV-15
European Proficiency Test FV-15

Potato

EURL
EUPT-FV-15

Organic Potatoes were grown in Almería, Spain

Post harvest treatment with commercial formulation and with standard solution

Commercial products used to treat the sample

Pesticide	Concentration (mg/kg)	MRRL	Type	Commercial Product
Acephate	<0.1	0.01	Standard	Dr.Ehrenstorfer
Azoxystrobin	0.1-0.2	0.01	Commercial	Ortiva 25% P/V
Chlorpropham	>1	0.01	Standard	Sigma-Aldrich
Chlorothalonil	0.1-0.5	0.01	Commercial	Bravo 50
Cypermethrin	<0.1	0.01	Commercial	Citron 10%
Diazinon	0.1-1	0.01	Commercial	Fegazinongole 60%
Fluopicolide	<0.1	0.01	Standard	Sigma-Aldrich
Flutolanil	0.1-0.5	0.01	Standard	ChemService
Fosthiazate	<0.1	0.01	Commercial	Nemathorin 10 G
Iprovalicarb	<0.1	0.01	Standard	Sigma-Aldrich
Linuron	<0.1	0.01	Standard	Sigma-Aldrich
Methiocarb	0.1-0.2	0.01	Standard	Dr.Ehrenstorfer
Pencycuron	0.1-1.0	0.01	Commercial	Trotis 25 sc
Prochloraz	<0.1	0.01	Standard	Sigma-Aldrich
Procymidone	<0.1	0.01	Commercial	Driza 50%
Spirodiclofen	0.1-1.0	0.01	Standard	Sigma-Aldrich
Thiabendazole	>1	0.01	Commercial	Textar 60T
Thiacloprid	0.1-0.5	0.01	Commercial	Calypso 48% P/V

Commercial products used to treat the sample

Pesticide	Concentration (mg/kg)	MRRL	Type	Commercial Product
Acephate	<0.1	0.01	Standard	Dr.Ehrenstorfer
Azoxystrobin	0.1-0.2	0.01	Commercial	Ortiva 25% P/V
Chlorpropham	>1	0.01	Standard	Sigma-Aldrich
Chlorthalonil	0.1-0.5	0.01	Commercial	Bravo 50
Cypermethrin	<0.1	0.01	Commercial	Citron 10%
Diazinon	0.1-1	0.01	Commercial	Fegazinongole 60%
Fluopicolide	<0.1	0.01	Standard	Sigma-Aldrich
Flutolanil	0.1-0.5	0.01	Standard	ChemService
Fosthiazate	<0.1	0.01	Commercial	Nemathorin 10 G
Iprovalicarb	<0.1	0.01	Standard	Sigma-Aldrich
Linuron	<0.1	0.01	Standard	Sigma-Aldrich
Methiocarb	0.1-0.2	0.01	Standard	Dr.Ehrenstorfer
Pencycuron	0.1-1.0	0.01	Commercial	Trotis 25 sc
Prochloraz	<0.1	0.01	Standard	Sigma-Aldrich
Procymidone	<0.1	0.01	Commercial	Driza 50%
Spirodiclofen	0.1-1.0	0.01	Standard	Sigma-Aldrich
Thiabendazole	>1	0.01	Commercial	Textar 60T
Thiacloprid	0.1-0.5	0.01	Commercial	Calypso 48% P/V


EUPT-Potato
EURL-FV
EUPT-Potato
EURL-FV


12:00
SERVICE ALERT
DHL
EXPRESS
12:00

Homogeneity

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

20 extracts

-The sampling standard deviation of all the pesticides must be lower than the critical value.

$$S_{sample}^2 < c$$

Homogeneity

Pesticide	Mean Conc. (mg/Kg)	Ss^2	c	$Ss^2 < c$ Pass/Fail
Acephate	0.066	3.06×10^{-6}	4.72×10^{-5}	Pass
Azoxystrobin	0.181	9.94×10^{-6}	3.60×10^{-4}	Pass
Chlorothalonil	0.211	-2.41×10^{-5}	5.60×10^{-4}	Pass
Chlorpropham	1.453	1.40×10^{-4}	2.85×10^{-2}	Pass
Cypermethrin	0.114	-3.46×10^{-6}	1.68×10^{-4}	Pass
Diazinon	0.181	-2.31×10^{-6}	4.44×10^{-4}	Pass
Fluopicolide	0.123	5.06×10^{-6}	1.70×10^{-4}	Pass
Flutolanil	0.336	-4.22×10^{-5}	1.47×10^{-3}	Pass
Fosthiazate	0.076	9.30×10^{-6}	6.46×10^{-5}	Pass
Iprovalicarb	0.084	5.95×10^{-6}	7.77×10^{-5}	Pass
Linuron	0.107	1.74×10^{-5}	1.43×10^{-4}	Pass
Methiocarb	0.139	2.54×10^{-5}	2.60×10^{-4}	Pass
Pencycuron	0.332	9.54×10^{-6}	1.21×10^{-3}	Pass
Prochloraz	0.048	4.22×10^{-7}	2.61×10^{-5}	Pass
Procymidone	0.120	5.34×10^{-6}	1.93×10^{-4}	Pass
Spirodiclofen	0.411	1.45×10^{-4}	2.22×10^{-3}	Pass
Thiabendazole	1.456	1.24×10^{-3}	2.30×10^{-2}	Pass
Thiacloprid	0.364	4.98×10^{-5}	1.57×10^{-3}	Pass

All the pesticides passed the homogeneity test

Homogeneity

Pesticide	Mean Conc. Homogeneity (mg/Kg)	Assigned value (mg/Kg)	Difference (%)
Acephate	0.066	0.083	20.5
Azoxystrobin	0.181	0.203	10.8
Chlorothalonil	0.211	0.160	-31.9
Chlorpropham	1.453	1.700	14.5
Cypermethrin	0.114	0.100	-14.0
Diazinon	0.181	0.195	7.2
Fluopicolide	0.123	0.099	-24.2
Flutolanil	0.336	0.410	18.0
Fosthiazate	0.076	0.080	5.0
Iprovalicarb	0.084	0.090	6.7
Linuron	0.107	0.098	-9.2
Methiocarb	0.139	0.136	-2.2
Pencycuron	0.332	0.269	-23,4
Prochloraz	0.048	0.058	17,2
Procymidone	0.120	0.110	-9,1
Spirodiclofen	0.411	0.444	7,4
Thiabendazole	1.456	1.710	14,9
Thiacloprid	0.364	0.338	-7,7

Stability

1st Analysis - prior to the sample shipment

2nd Analysis - after the deadline for reporting results

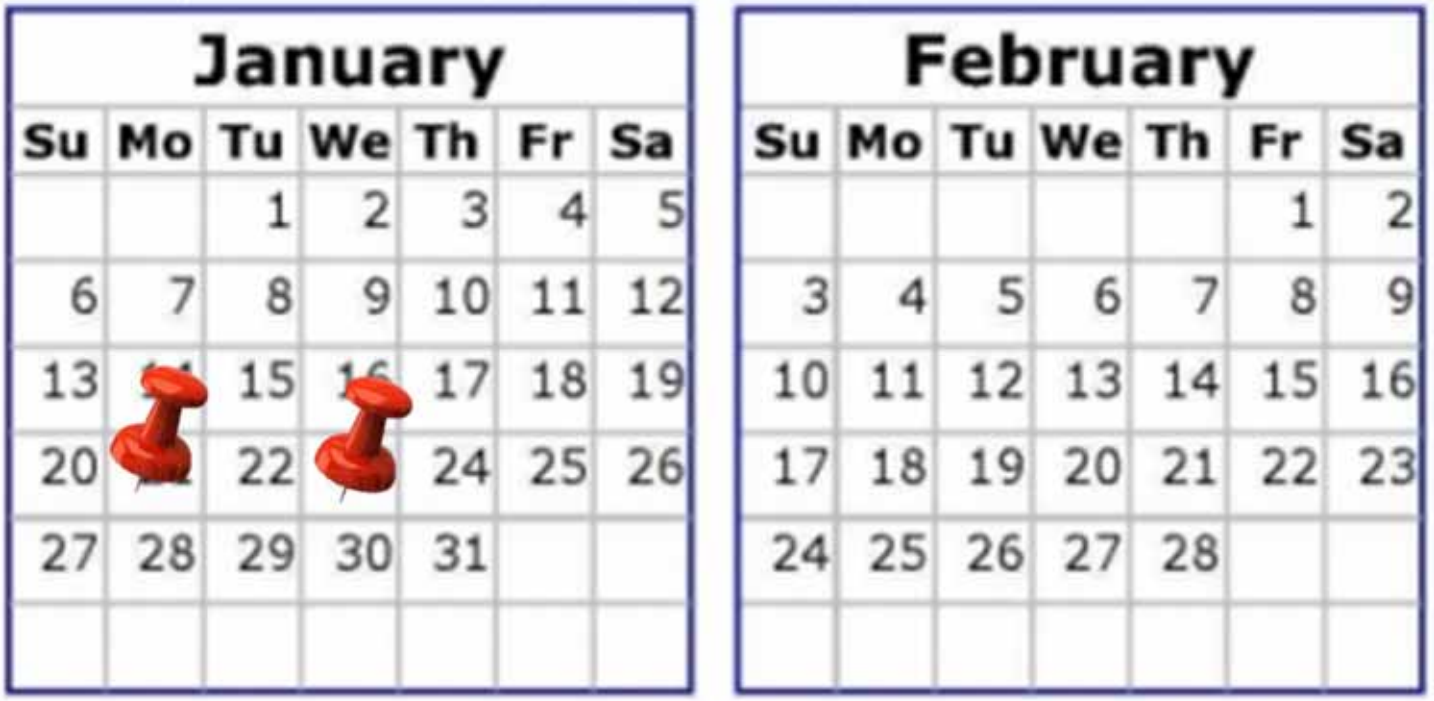
Stability

Pesticide	Concentration (mg/kg)							
	Day 1 (1st analysis)	Day 1 (2nd analysis)	Mean 1	Day 2 (1st analysis)	Day 2 (2nd analysis)	Mean 2	(M2-M1) M1	%
Acephate	0.051	0.069	0.060	0.061	0.067	0.064	0.067	7
Azoxystrobin	0.159	0.158	0.159	0.171	0.176	0.174	0.095	9
Chlorothalonil	0.214	0.218	0.216	0.221	0.235	0.228	0.056	6
Chlo								1
Cype								-1
Diazi								3
Fluopicolide	0.127	0.127	0.127	0.126	0.129	0.128	0.004	0
Flutolanil	0.321	0.331	0.326	0.325	0.323	0.324	-0.006	-1
Fosthiazate	0.061	0.059	0.060	0.061	0.065	0.063	0.050	5
Iprovalicarb	0.081	0.079	0.080	0.092	0.091	0.092	0.144	14
Linuron	0.093	0.087	0.090	0.088	0.086	0.087	-0.033	-3
Methiocarb	0.137	0.148	0.143	0.136	0.135	0.136	-0.049	-5
Pencycuron	0.327	0.321	0.324	0.370	0.369	0.370	0.140	14
Prochloraz	0.049	0.049	0.049	0.050	0.051	0.051	0.031	3
Procymidone	0.120	0.124	0.122	0.127	0.126	0.127	0.037	4
Spirodiclofen	0.443	0.451	0.447	0.438	0.441	0.440	-0.017	-2
Thiabendazole	1.245	1.259	1.252	1.375	1.385	1.380	0.102	10
Thiacloprid	0.295	0.292	0.294	0.306	0.310	0.308	0.049	5

All the pesticides passed the stability test

Stability

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

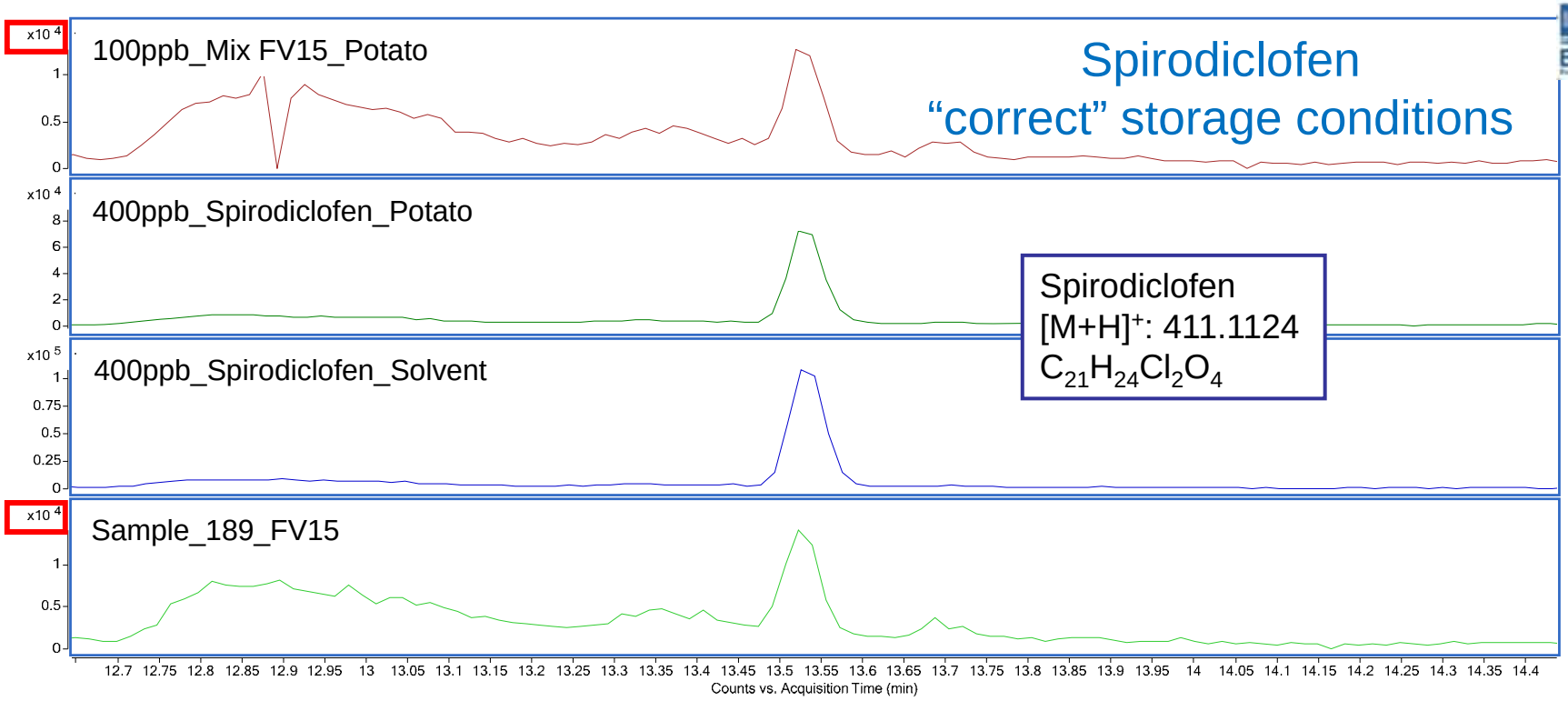


Stability

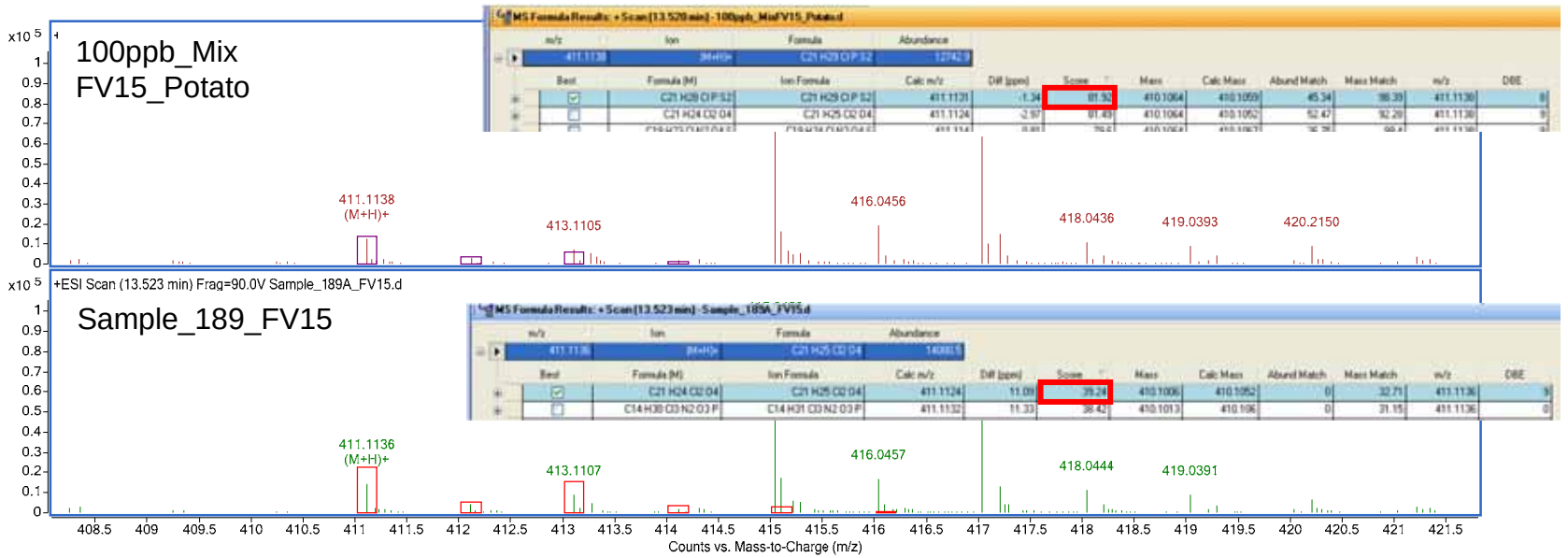
Pesticide	Concentration (mg/kg)							
	Day 1 (1st analysis)	Day 1 (2nd analysis)	Mean 1	48h (1st analysis)	48h (2nd analysis)	Mean 2	(M2-M1) M1	%
Acephate	0.051	0.069	0.060	0.062	0.057	0.060	-0.008	-1
Azoxystrobin	0.159	0.158	0.159	0.169	0.164	0.167	0.050	5
Chlorothalonil	0.214	0.218	0.216	0.201	0.219	0.210	-0.028	-3
Chlor								3
Cyper								-8
Diazinon	0.166	0.183	0.175	0.180	0.171	0.176	0.006	1
Fluopicolide	0.127	0.127	0.127	0.130	0.127	0.129	0.012	1
Flutolanil	0.321	0.331	0.326	0.323	0.309	0.316	-0.031	-3
Fosthiazate	0.061	0.059	0.060	0.065	0.063	0.064	0.067	7
Iprovalicarb	0.081	0.079	0.080	0.086	0.082	0.084	0.050	5
Linuron	0.093	0.087	0.090	0.084	0.085	0.085	-0.061	-6
Methiocarb	0.137	0.148	0.143	0.144	0.135	0.140	-0.021	-2
Pencycuron	0.327	0.321	0.324	0.347	0.328	0.338	0.042	4
Prochloraz	0.049	0.049	0.049	0.053	0.050	0.052	0.051	5
Procymidone	0.120	0.124	0.122	0.123	0.117	0.120	-0.016	-2
Spirodiclofen	0.443	0.451	0.447	0.431	0.410	0.421	-0.059	-6
Thiabendazole	1.245	1.259	1.252	1.355	1.328	1.342	0.071	7
Thiacloprid	0.295	0.292	0.294	0.323	0.311	0.317	0.080	8

All the pesticides passed the stability test

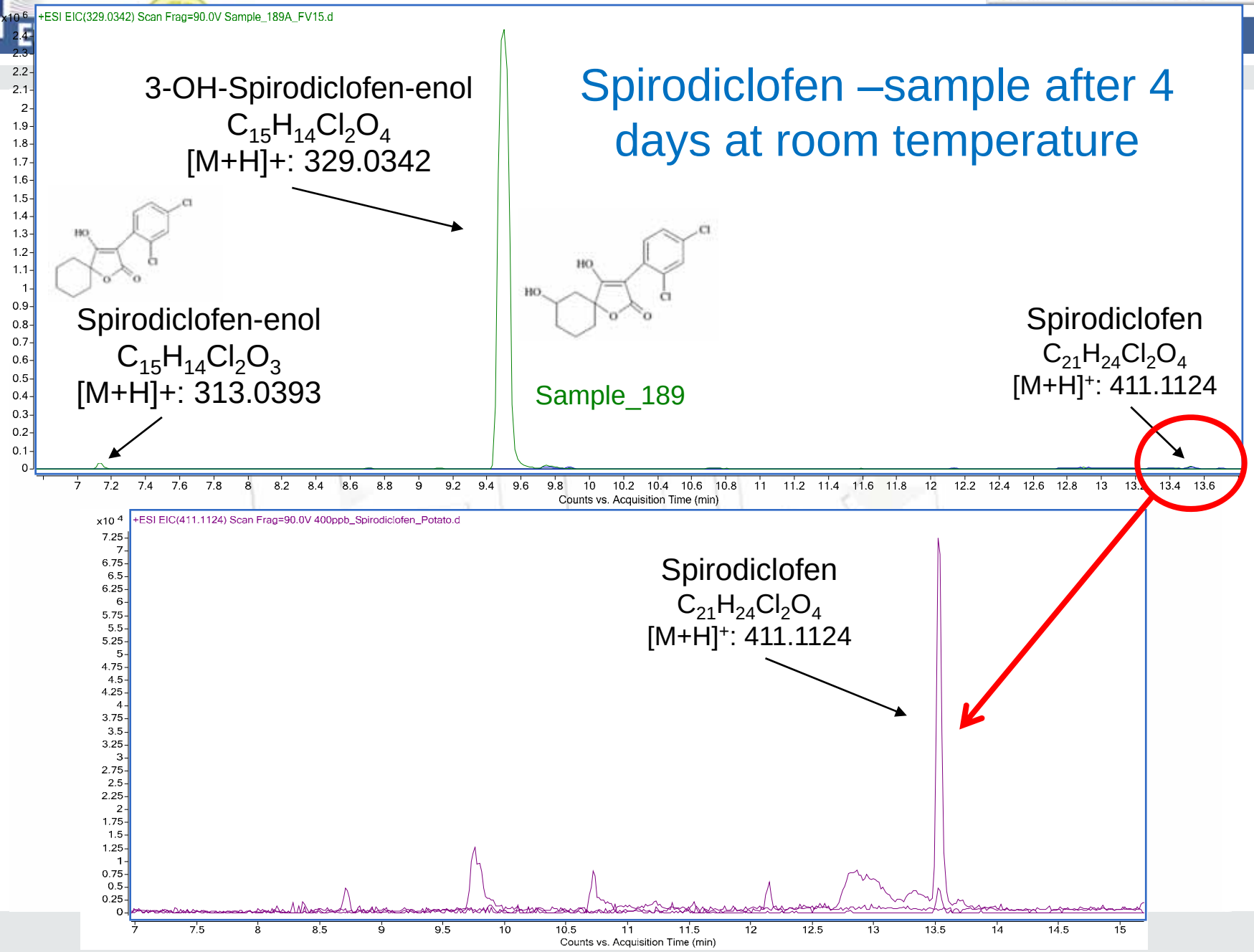
Spirodiclofen
“correct” storage conditions

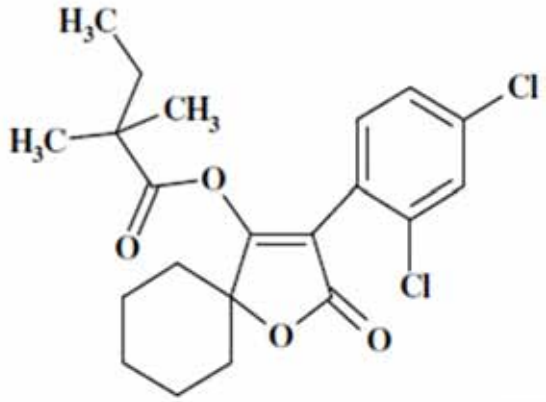


Spirodiclofen
$[M+H]^+$: 411.1124
$C_{21}H_{24}Cl_2O_4$

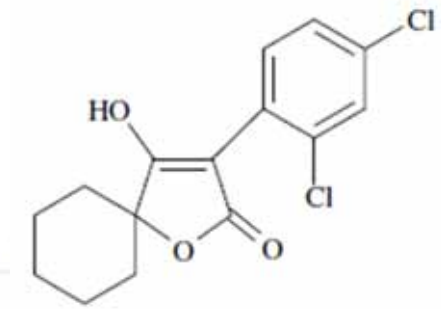


Spirodiclofen –sample after 4 days at room temperature

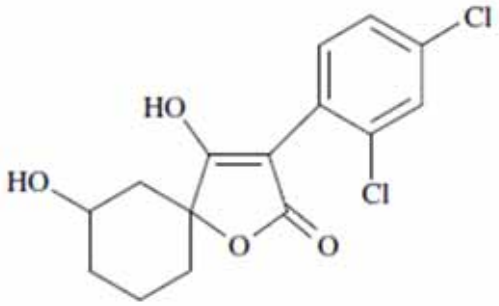




Spirodiclofen

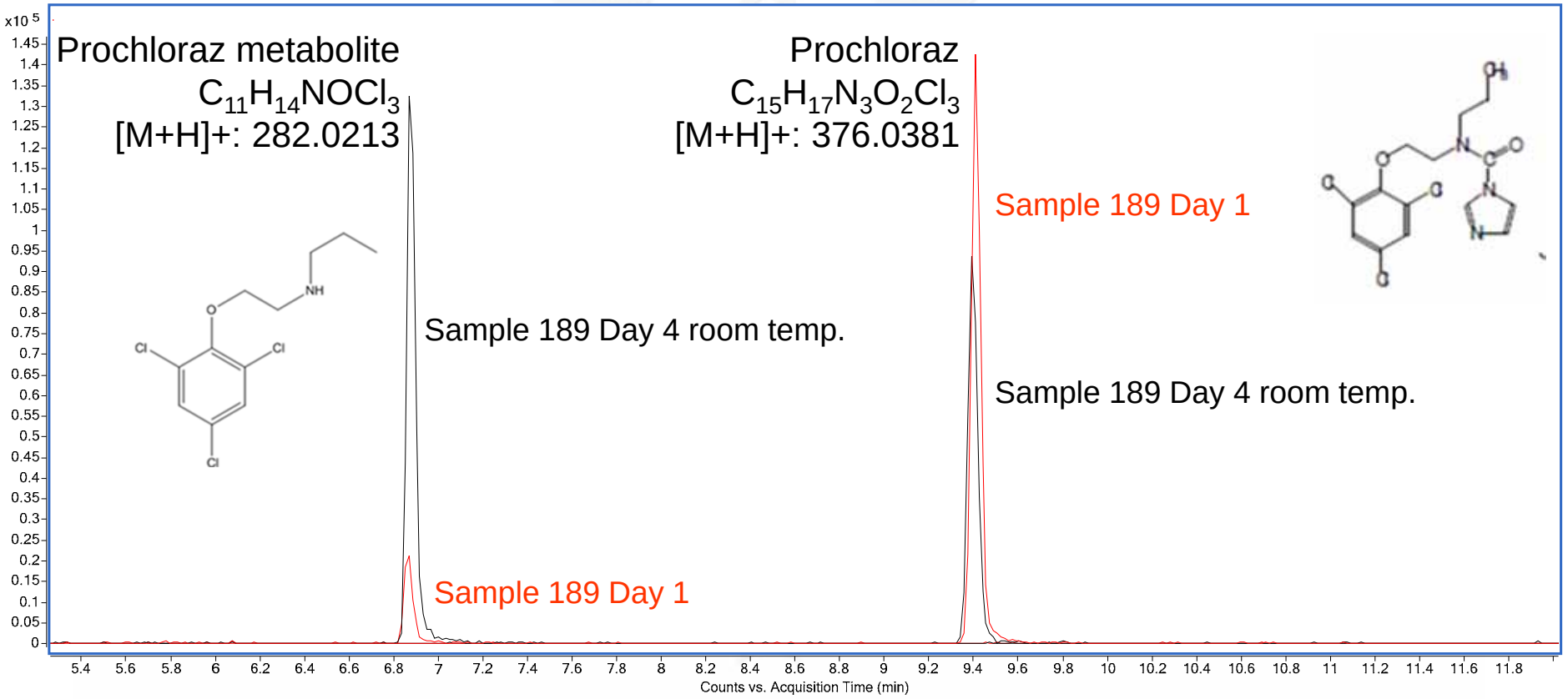


Spirodiclofen-enol



3-hydroxy-spirodiclofen-enol

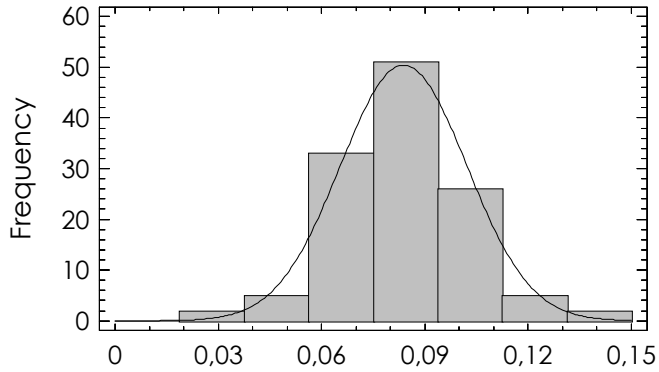
PROCHLORAZ- Potato sample at room temperature during 4 days



RESULTS

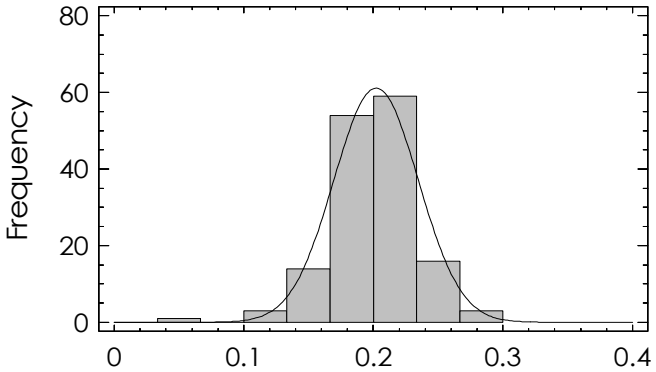
Distribution of data-Histograms

Acephate



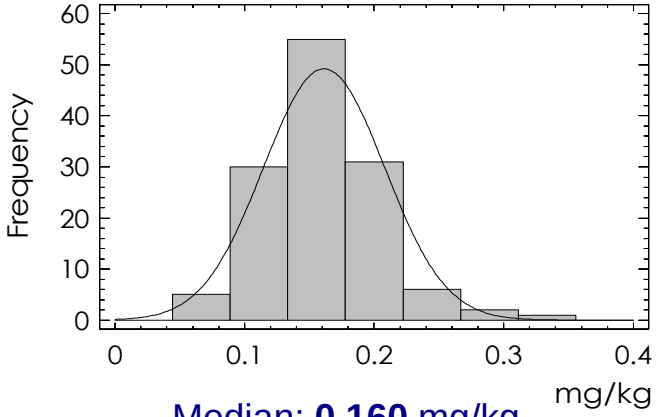
Median: **0.083** mg/kg

Azoxystrobin



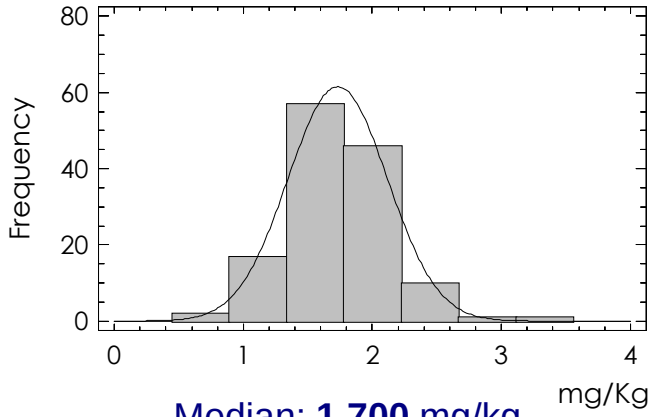
Median: **0.203** mg/kg

Chlorothalonil



Median: **0.160** mg/kg

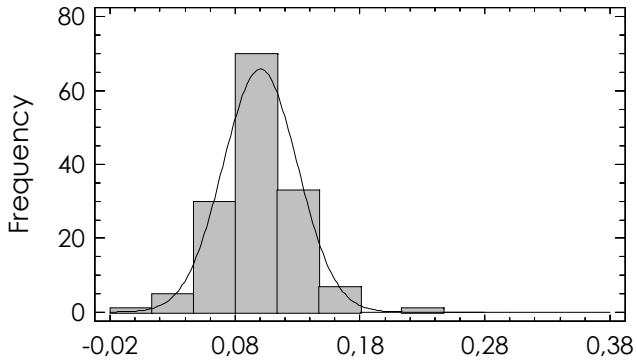
Chlorpropham



Median: **1.700** mg/kg

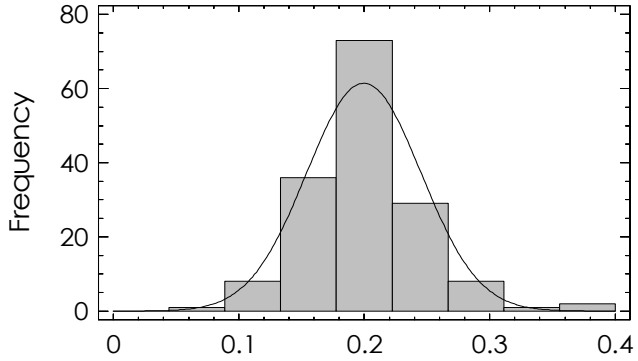
Distribution of data-Histograms

Cypermethrin



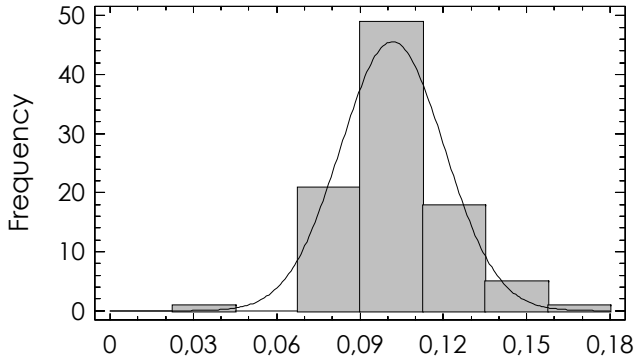
Median: **0.100** mg/kg

Diazinon



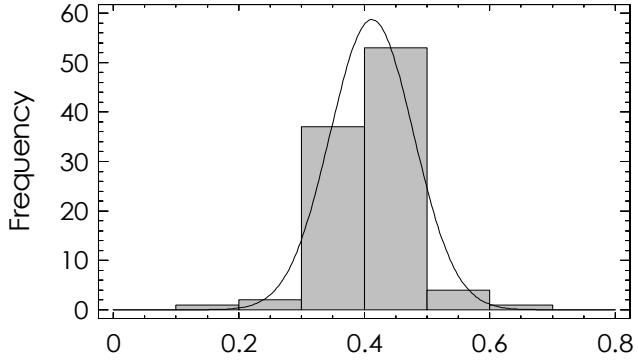
Median: **0.195** mg/kg

Fluopicolide



Median: **0.099** mg/kg

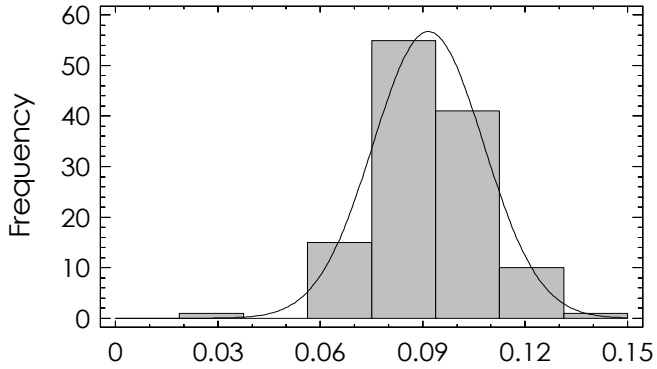
Flutolanil



Median: **0.410** mg/kg

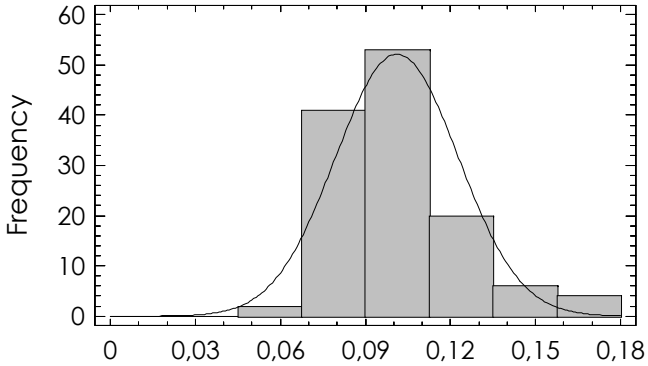
Distribution of data-Histograms

Iprovalicarb



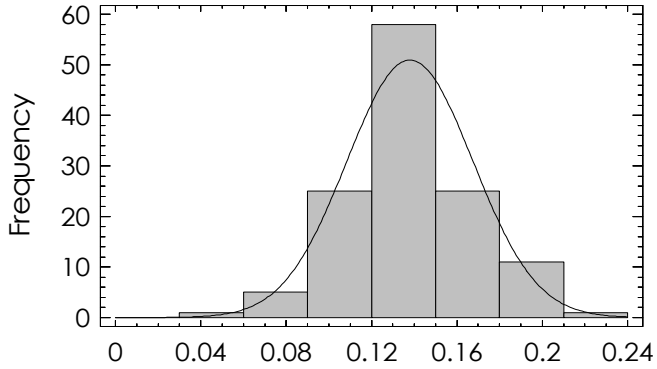
Median: **0.090** mg/kg

Linuron



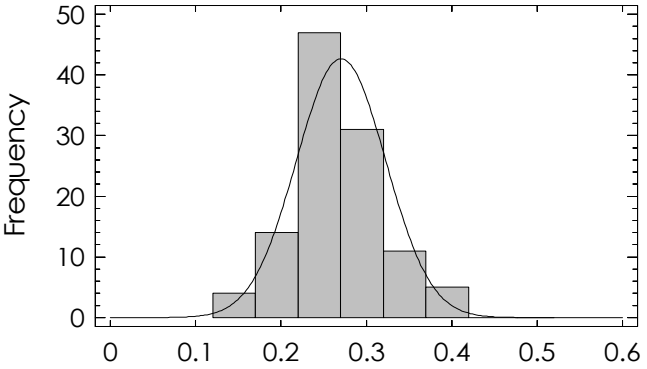
Median: **0.098** mg/kg

Methiocarb



Median: **0.136** mg/kg

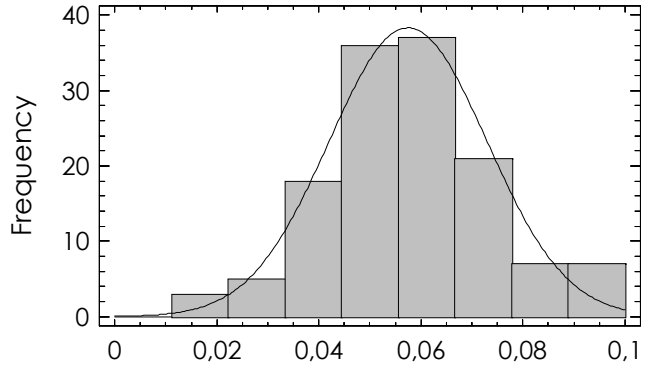
Pencycuron



Median: **0.269** mg/kg

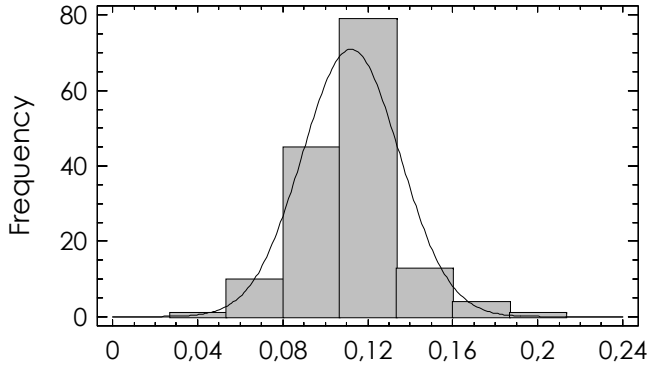
Distribution of data-Histograms

Prochloraz



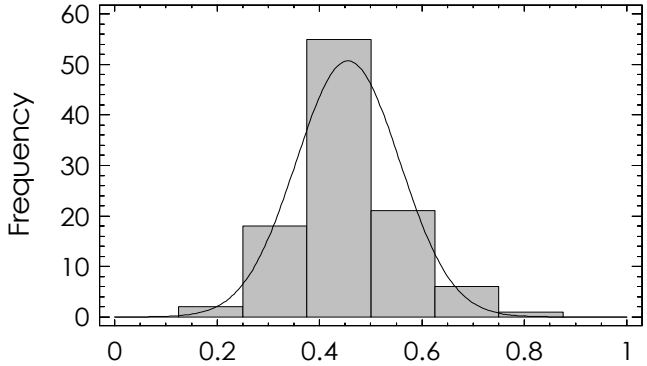
Median: **0.058** mg/kg mg/Kg

Procymidone



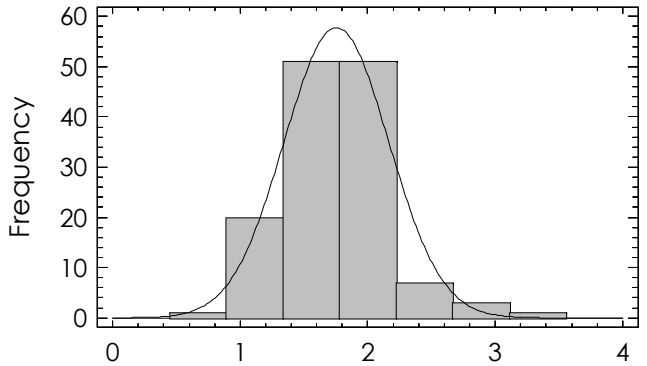
Median: **0.110** mg/kg mg/Kg

Spirodiclofen



Median: **0.444** mg/kg mg/kg

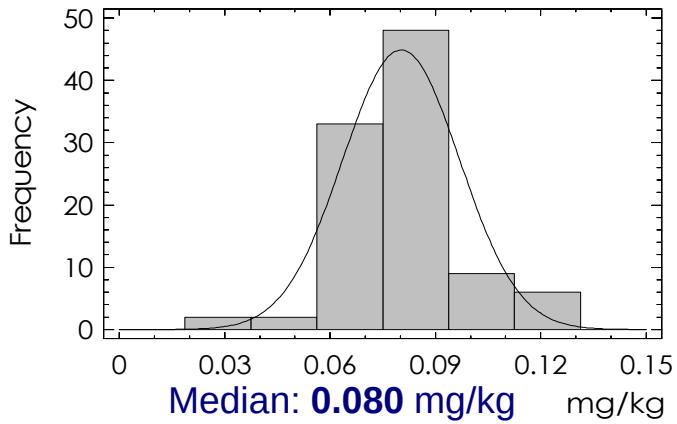
Thiabendazole



Median: **1.710** mg/kg mg/Kg

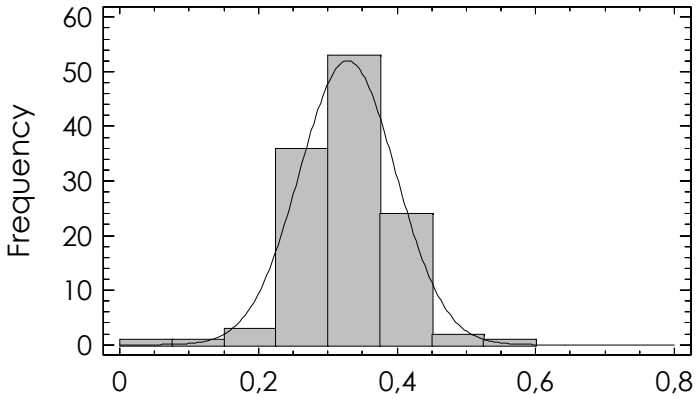
Distribution of data-Histograms

Fosthiazate



Median: **0.080** mg/kg

Thiacloprid



Median: **0.338** mg/kg

Pesticides	Median (mg/kg)
Prochloraz	0.058
Fosthiazate	0.080
Acephate	0.083
Iprovalicarb	0.090
Linuron	0.098
Fluopicolide	0.099
Cypermethrin	0.100
Procymidone	0.110
Methiocarb	0.136
Chlorothalonil	0.160
Diazinon	0.195
Azoxystrobin	0.203
Pencycuron	0.269
Thiacloprid	0.338
Flutolanil	0.410
Spirodiclofen	0.444
Chlorpropham	1.700
Thiabendazole	1.710

Pesticides	Median (mg/kg)
Prochloraz	0.058
Fosthiazate	0.080
Acephate	0.083
Iprovalicarb	0.090
Linuron	0.098
Fluopicolide	0.099
Cypermethrin	0.100
Procymidone	0.110
Methiocarb	0.136
Chlorothalonil	0.160
Diazinon	0.195
Azoxystrobin	0.203
Pencycuron	0.269
Thiacloprid	0.338
Flutolanil	0.410
Spirodiclofen	0.444
Chlorpropham	1.700
Thiabendazole	1.710

0.058-0.100 mg/kg

Pesticides	Median (mg/kg)
Prochloraz	0.058
Fosthiazate	0.080
Acephate	0.083
Iprovalicarb	0.090
Linuron	0.098
Fluopicolide	0.099
Cypermethrin	0.100
Procymidone	0.110
Methiocarb	0.136
Chlorothalonil	0.160
Diazinon	0.195
Azoxystrobin	0.203
Pencycuron	0.269
Thiacloprid	0.338
Flutolanil	0.410
Spirodiclofen	0.444
Chlorpropham	1.700
Thiabendazole	1.710

0.058-0.100 mg/kg

0.100-0.500 mg/kg

EURL-FV

EUPT-FV-15
European Proficiency Test FV-15

Pesticides	Median (mg/kg)
Prochloraz	0.058
Fosthiazate	0.080
Acephate	0.083
Iprovalicarb	0.090
Linuron	0.098
Fluopicolide	0.099
Cypermethrin	0.100
Procymidone	0.110
Methiocarb	0.136
Chlorothalonil	0.160
Diazinon	0.195
Azoxystrobin	0.203
Pencycuron	0.269
Thiacloprid	0.338
Flutolanil	0.410
Spirodiclofen	0.444
Chlorpropham	1.700
Thiabendazole	1.710

0.058-0.100 mg/kg

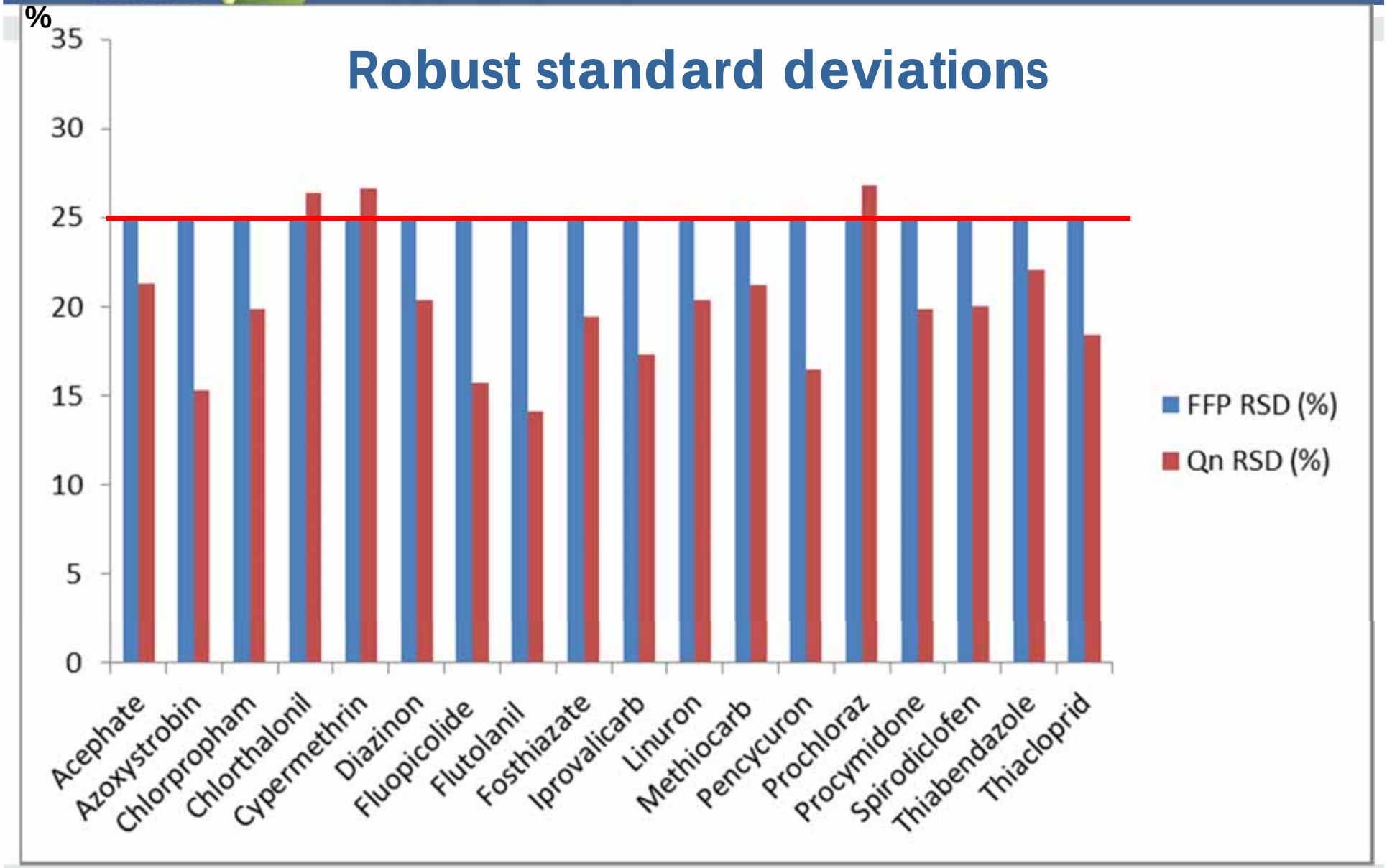
0.100-0.500 mg/kg

0.500-2.000 mg/kg

EUPT-FV-15
European Proficiency Test FV-15

Pesticides	MRRL (mg/kg)	Median (mg/kg)	FFP RSD (%)	Qn RSD (%)
Acephate	0.01	0.083	25	21.3
Azoxystrobin	0.01	0.203	25	15.3
Chlorothalonil	0.01	0.160	25	26.4
Chlorpropham	0.01	1.700	25	19.9
Cypermethrin	0.01	0.100	25	26.6
Diazinon	0.01	0.195	25	20.4
Fluopicolide	0.01	0.099	25	15.7
Flutolanil	0.01	0.410	25	14.1
Fosthiazate	0.01	0.080	25	19.4
Iprovalicarb	0.01	0.090	25	17.3
Linuron	0.01	0.098	25	20.4
Methiocarb	0.01	0.136	25	21.2
Pencycuron	0.01	0.269	25	16.5
Prochloraz	0.01	0.058	25	26.8
Procymidone	0.01	0.110	25	19.9
Spirodiclofen	0.01	0.444	25	20.0
Thiabendazole	0.01	1.710	25	22.1
Thiacloprid	0.01	0.338	25	18.4

Robust standard deviations

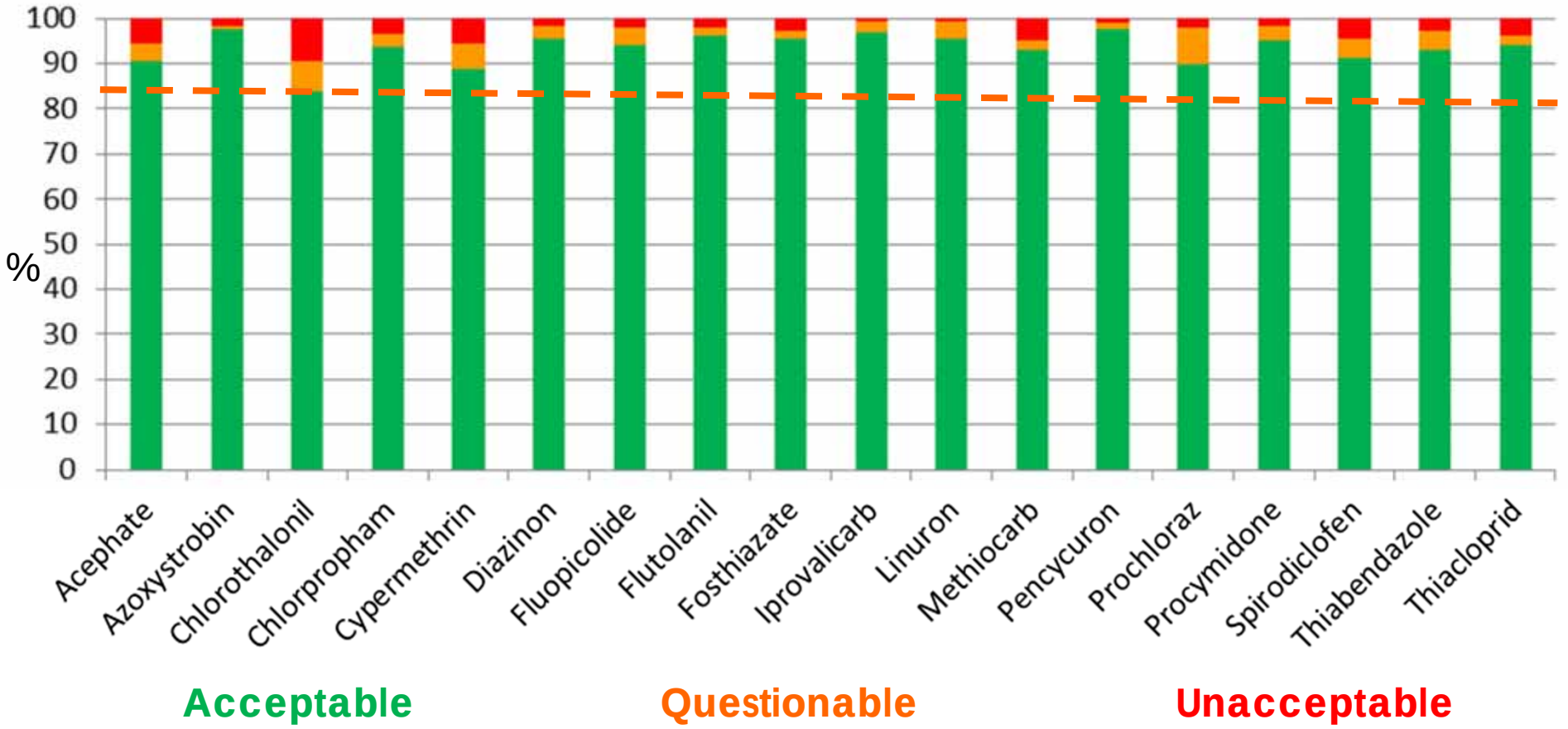


EUPT-FV-15
European Proficiency Test FV-15

Pesticides	No. of Reported Results	No. of False Negative Results	No. of Not Analysed Results	Percentage of Reported Results (out of 160)
Acephate	124	8	28	78
Azoxystrobin	151	1	8	94
Chlorothalonil	134	5	21	84
Chlorpropham	134	3	23	84
Cypermethrin	146	6	8	91
Diazinon	159	0	1	99
Fluopicolide	95	0	65	59
Flutolanil	99	1	60	62
Fosthiazate	101	1	58	63
Iprovalicarb	124	0	36	78
Linuron	126	1	33	79
Methiocarb	128	4	28	80
Pencycuron	113	0	47	71
Prochloraz	134	3	23	84
Procymidone	153	1	6	96
Spirodiclofen	105	2	53	66
Thiabendazole	134	1	25	84
Thiachloprid	121	2	37	76

z-Scores

z-Scores classification



Acceptable **Questionable** **Unacceptable**

EUPT-FV-15
European Proficiency Test FV-15

Pesticides	Median (mg/kg)	Acceptable (%)	Questionable (%)	Unacceptable (%)
Acephate	0.083	90.1	3.8	6.1
Azoxystrobin	0.203	98.0	0.7	1.3
Chlorothalonil	0.160	83.5	7.2	9.3
Chlorpropham	1.700	93.4	3.0	3.6
Cypermethrin	0.100	89.4	6.0	4.6
Diazinon	0.195	95.0	3.1	1.9
Fluopicolide	0.099	95.7	4.3	0.0
Flutolanil	0.410	96.0	2.0	2.0
Fosthiazate	0.080	96.0	2.0	2.0
Iprovalicarb	0.090	97.6	1.6	0.8
Linuron	0.098	95.2	4.0	0.8
Methiocarb	0.136	93.1	2.3	4.6
Pencycuron	0.269	97.3	1.8	0.9
Prochloraz	0.058	89.7	8.1	2.2
Procymidone	0.110	94.8	3.3	1.9
Spirodiclofen	0.444	90.6	4.7	4.7
Thiabendazole	1.710	95.6	3.0	1.4
Thiacloprid	0.338	95.0	2.5	2.5

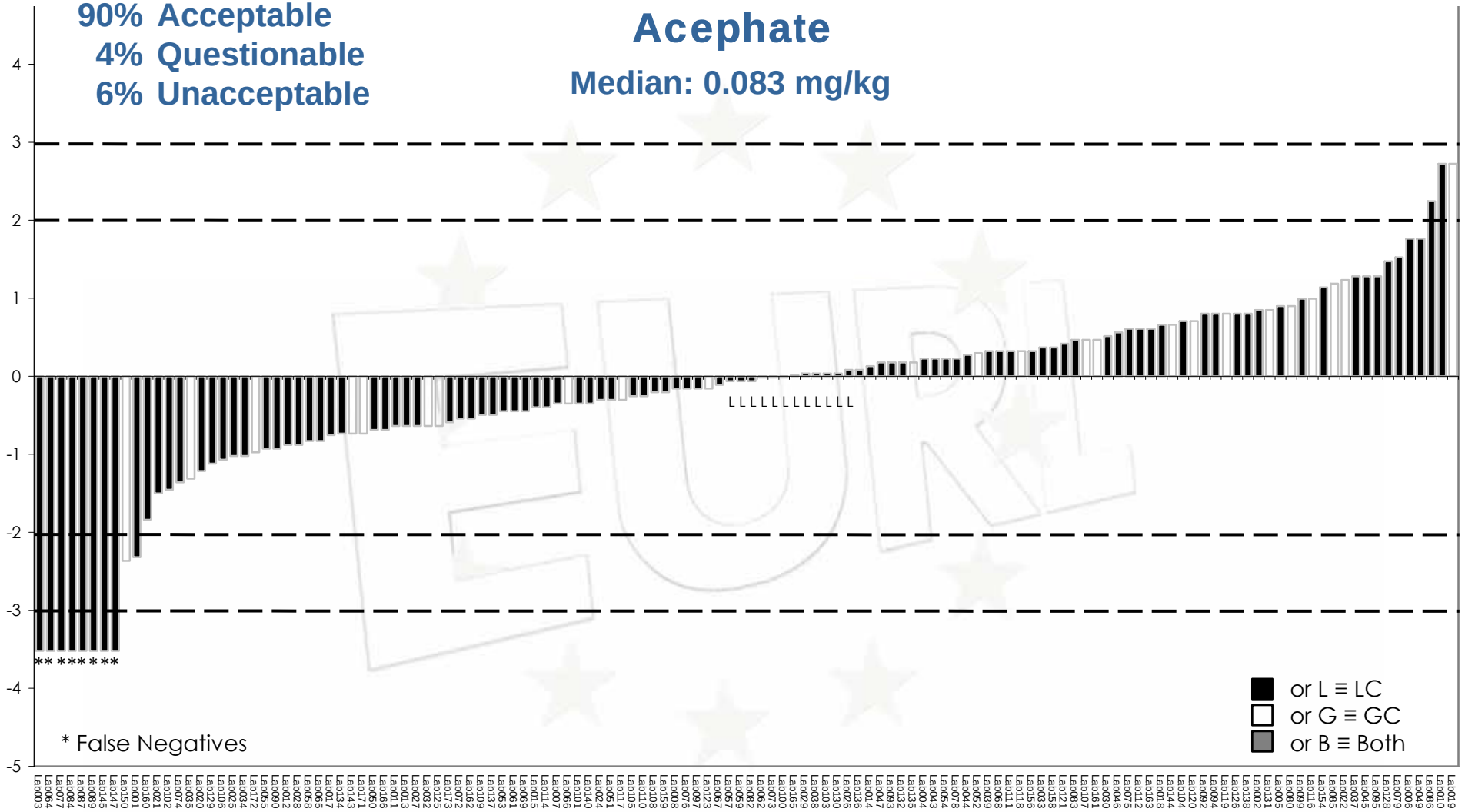
EUPT-FV-15
European Proficiency Test FV-15

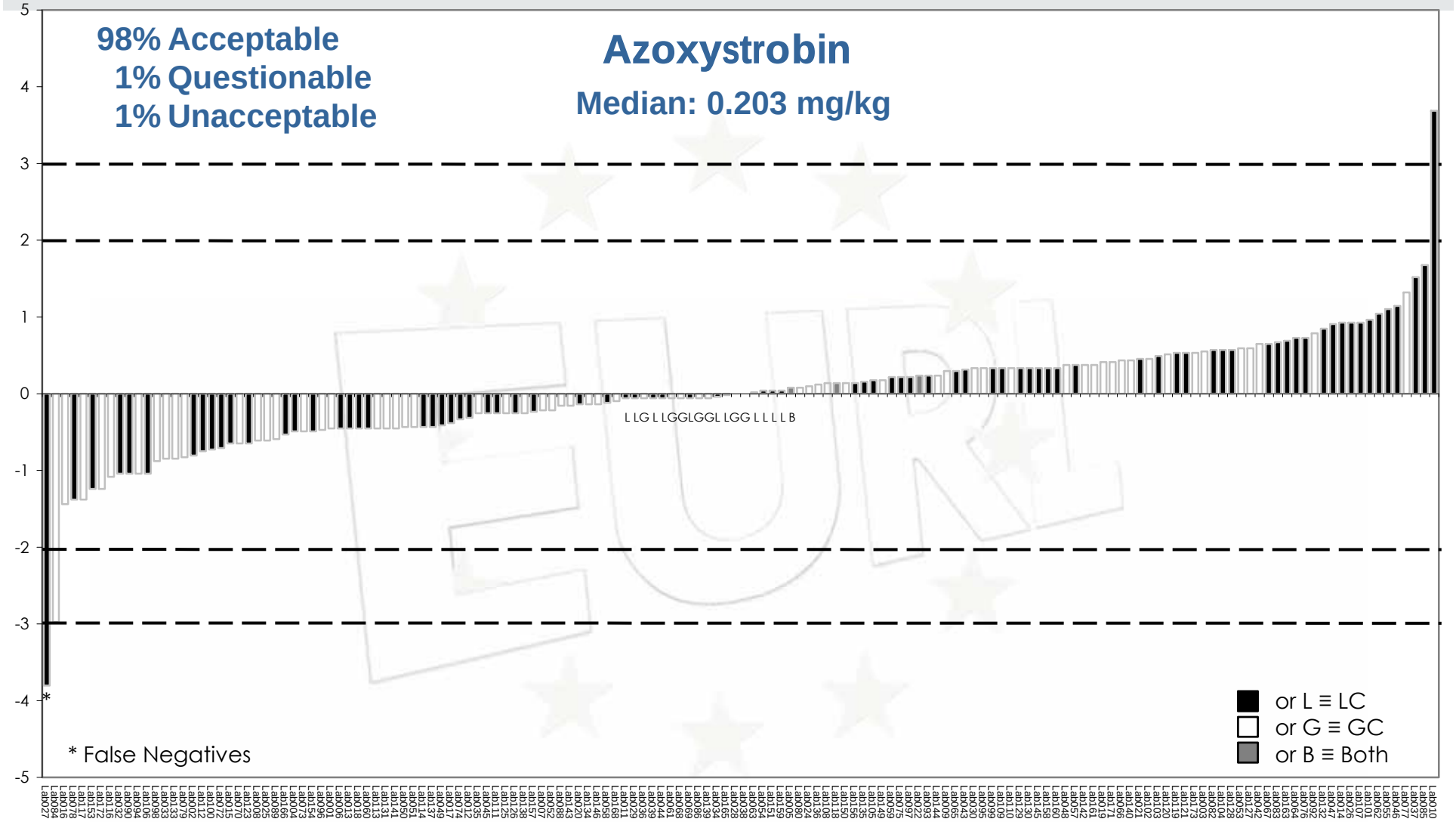
Pesticides	Median (mg/kg)	Acceptable (%)	Questionable (%)	Unacceptable (%)
Acephate	0.083	90.1	3.8	6.1
Azoxystrobin	0.203	98.0	0.7	1.3
Chlorothalonil	0.160	83.5	7.2	9.3
Chlorpropham	1.700	93.4	3.0	3.6
Cypermethrin	0.100	89.4	6.0	4.6
Diazinon	0.195	95.0	3.1	1.9
Fluopicolide	0.099	95.7	4.3	0.0
Flutolanil	0.410	96.0	2.0	2.0
Fosthiazate	0.080	96.0	2.0	2.0
Iprovalicarb	0.090	97.6	1.6	0.8
Linuron	0.098	95.2	4.0	0.8
Methiocarb	0.136	93.1	2.3	4.6
Pencycuron	0.269	97.3	1.8	0.9
Prochloraz	0.058	89.7	8.1	2.2
Procymidone	0.110	94.8	3.3	1.9
Spirodiclofen	0.444	90.6	4.7	4.7
Thiabendazole	1.710	95.6	3.0	1.4
Thiacloprid	0.338	95.0	2.5	2.5

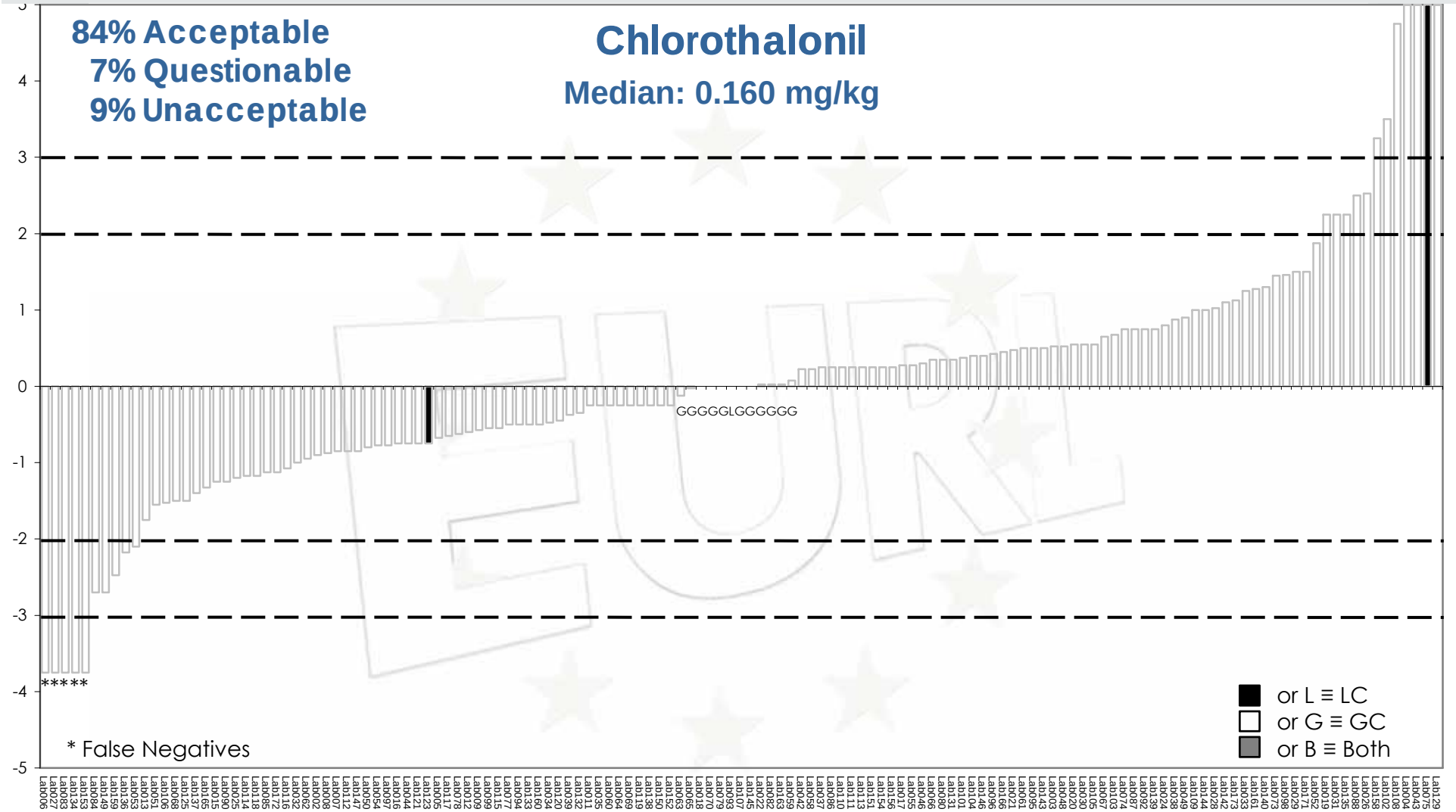
90% Acceptable
4% Questionable
6% Unacceptable

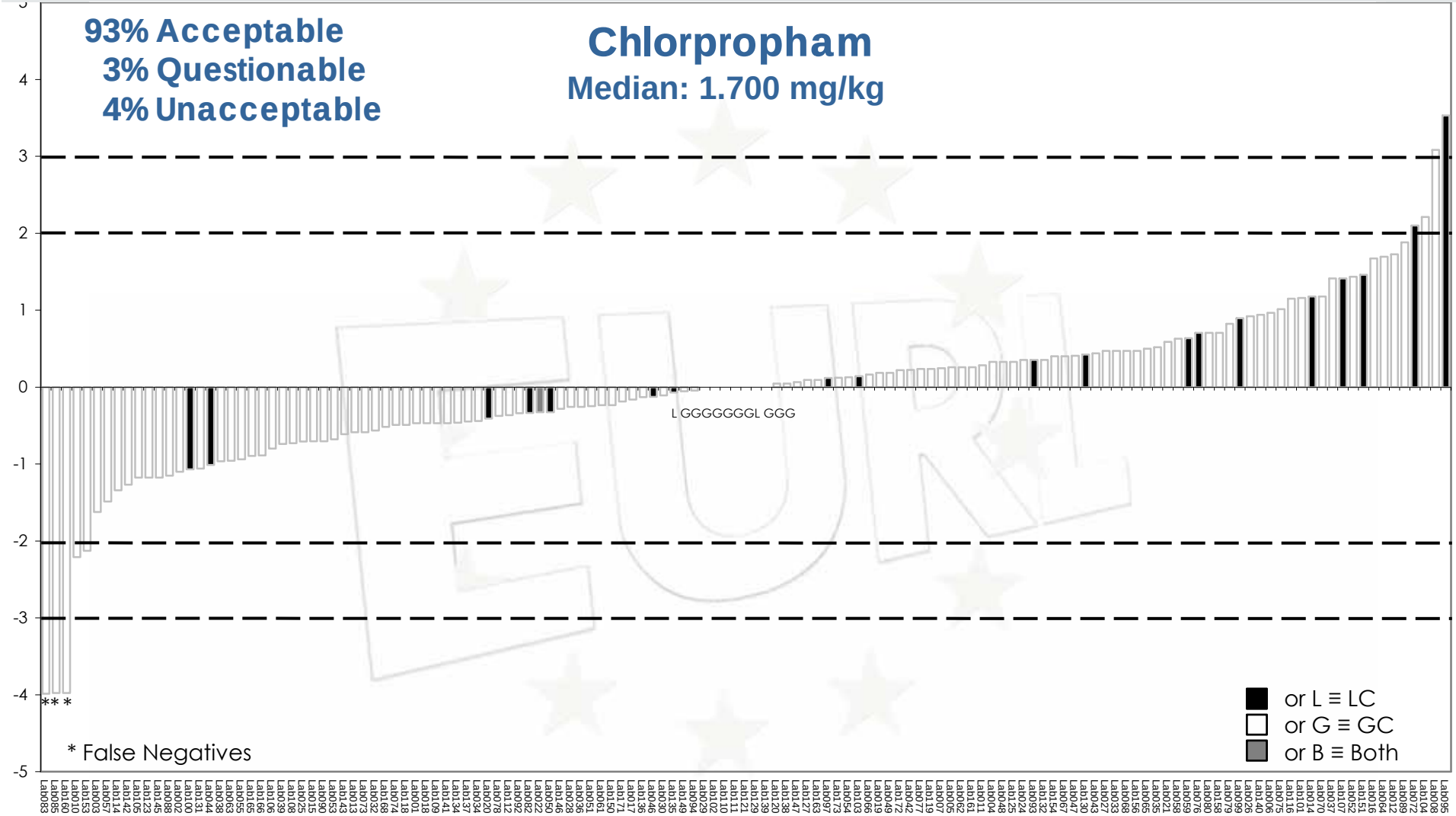
Acephate

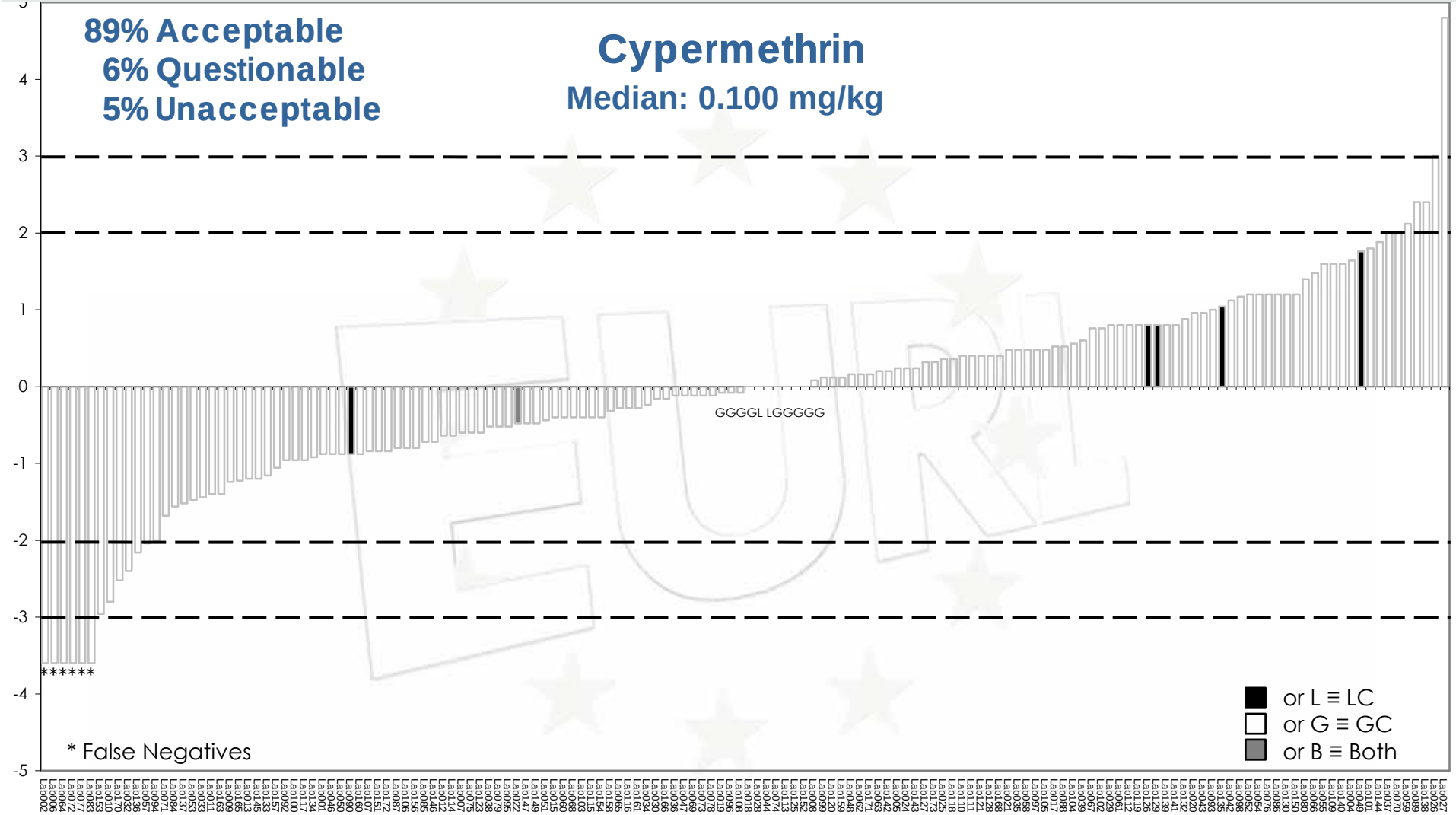
Median: 0.083 mg/kg

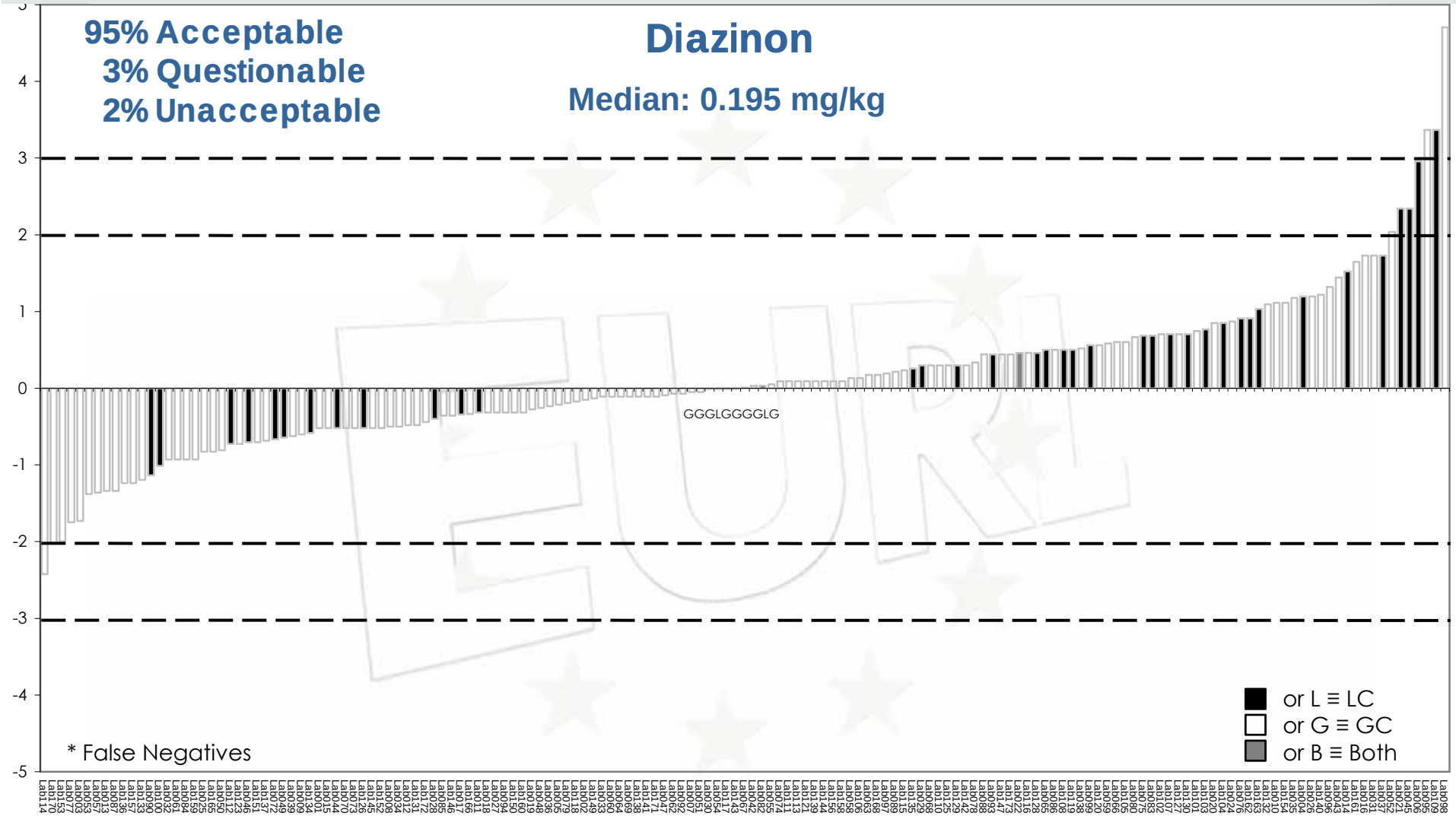


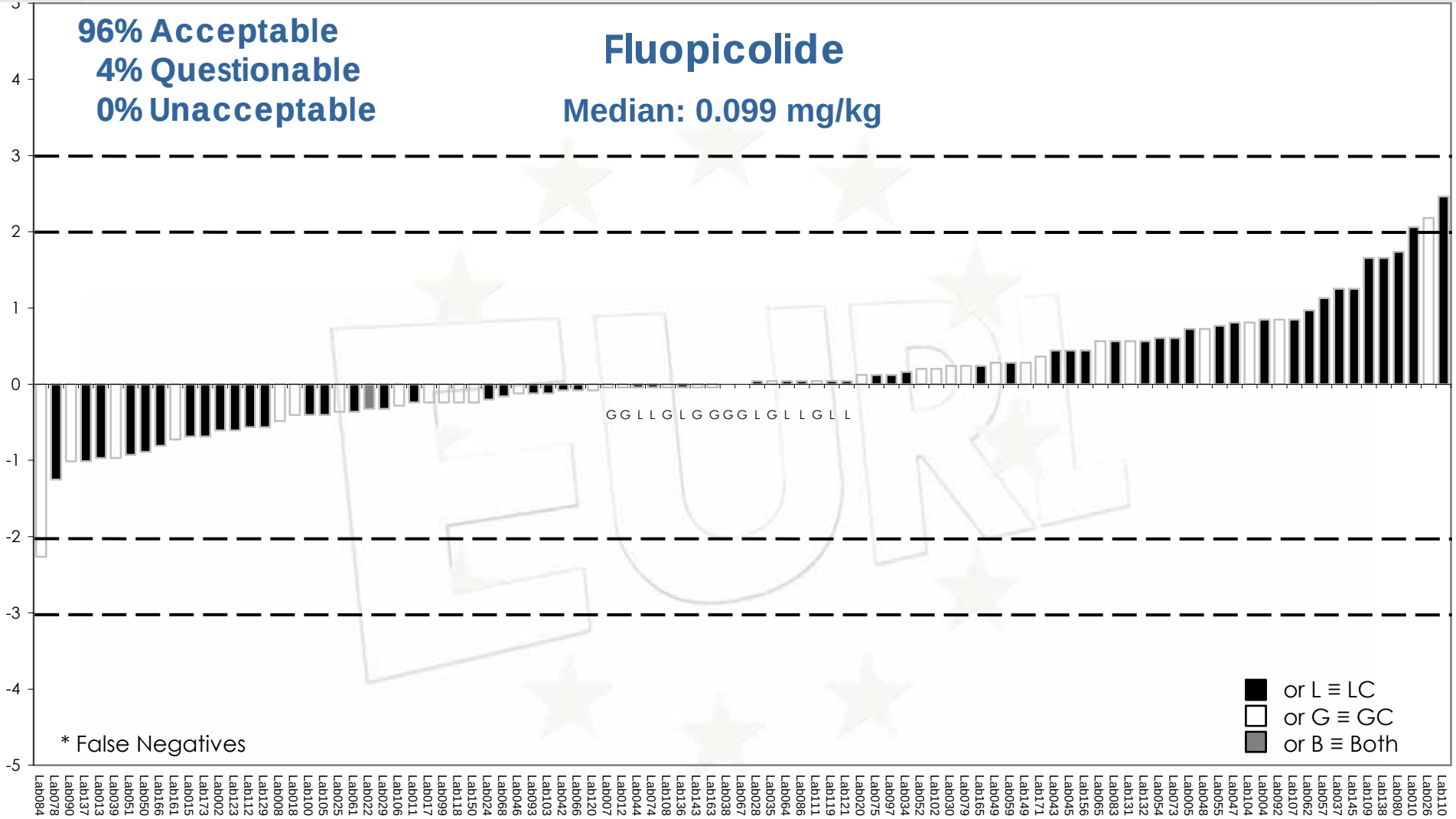

98% Acceptable
1% Questionable
1% Unacceptable
Azoxystrobin
Median: 0.203 mg/kg
5
4
3
2
1
0
-1
-2
-3
-4
-5
L LG L LGGLGGL LGG L L L L B
*
* False Negatives
or L ≡ LC
or G ≡ GC
or B ≡ Both

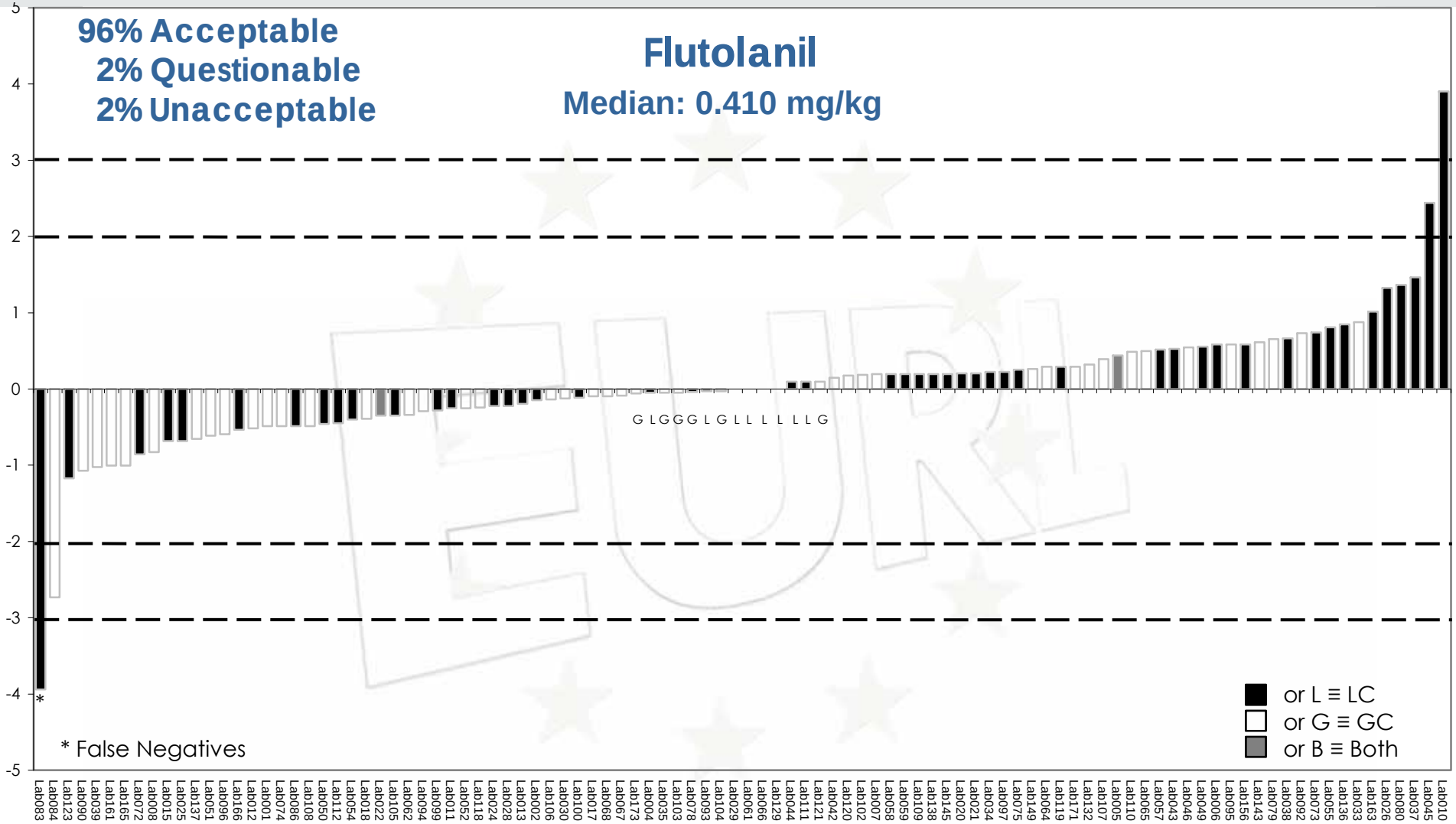

84% Acceptable
7% Questionable
9% Unacceptable
Chlorothalonil
Median: 0.160 mg/kg
GGGGGLGGGGGG
*****
* False Negatives
or L ≡ LC
or G ≡ GC
or B ≡ Both

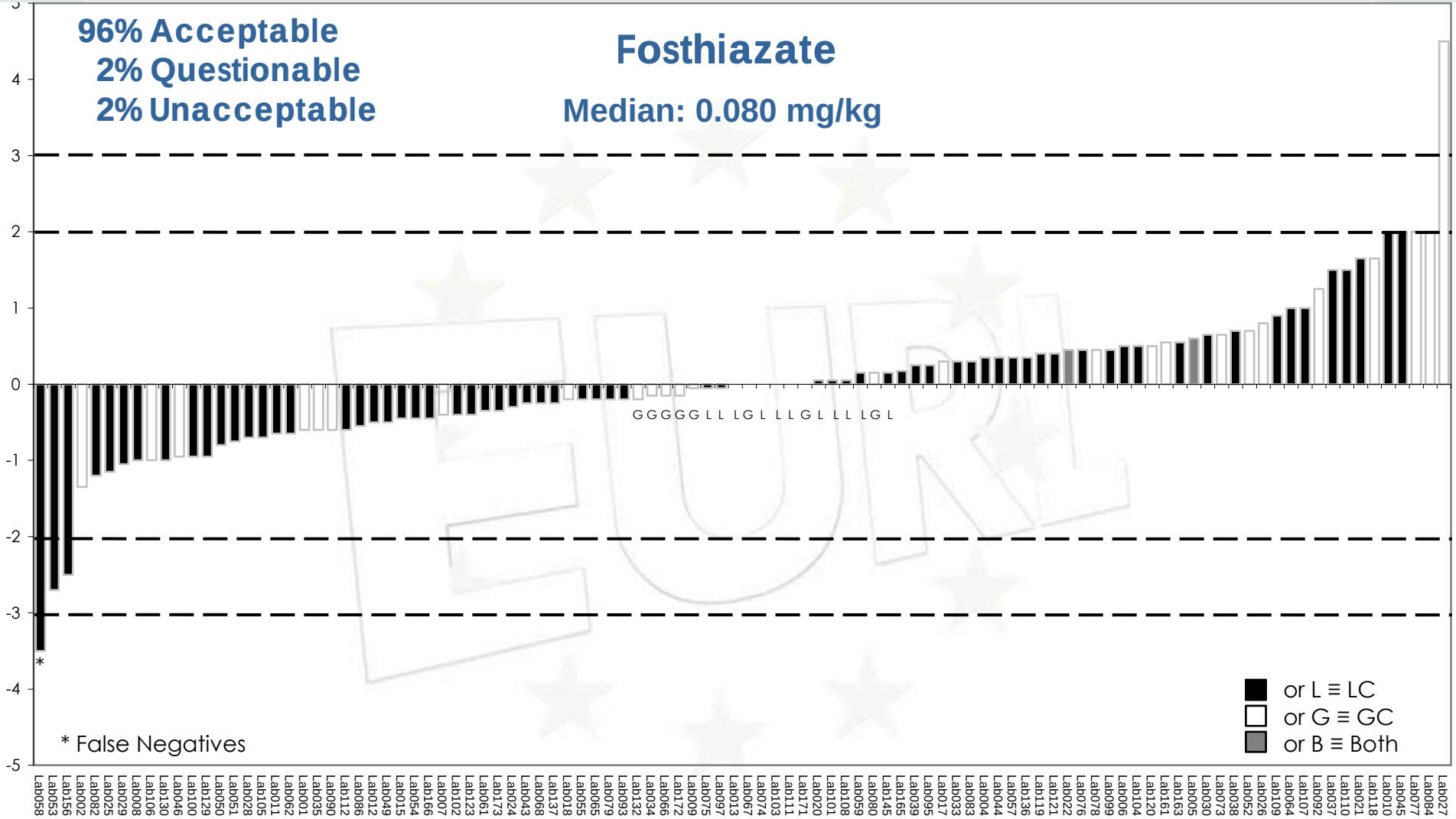

93% Acceptable
3% Questionable
4% Unacceptable
Chlorpropham
Median: 1.700 mg/kg
L GGGGGGGL GGG
***
* False Negatives
or L ≡ LC
or G ≡ GC
or B ≡ Both

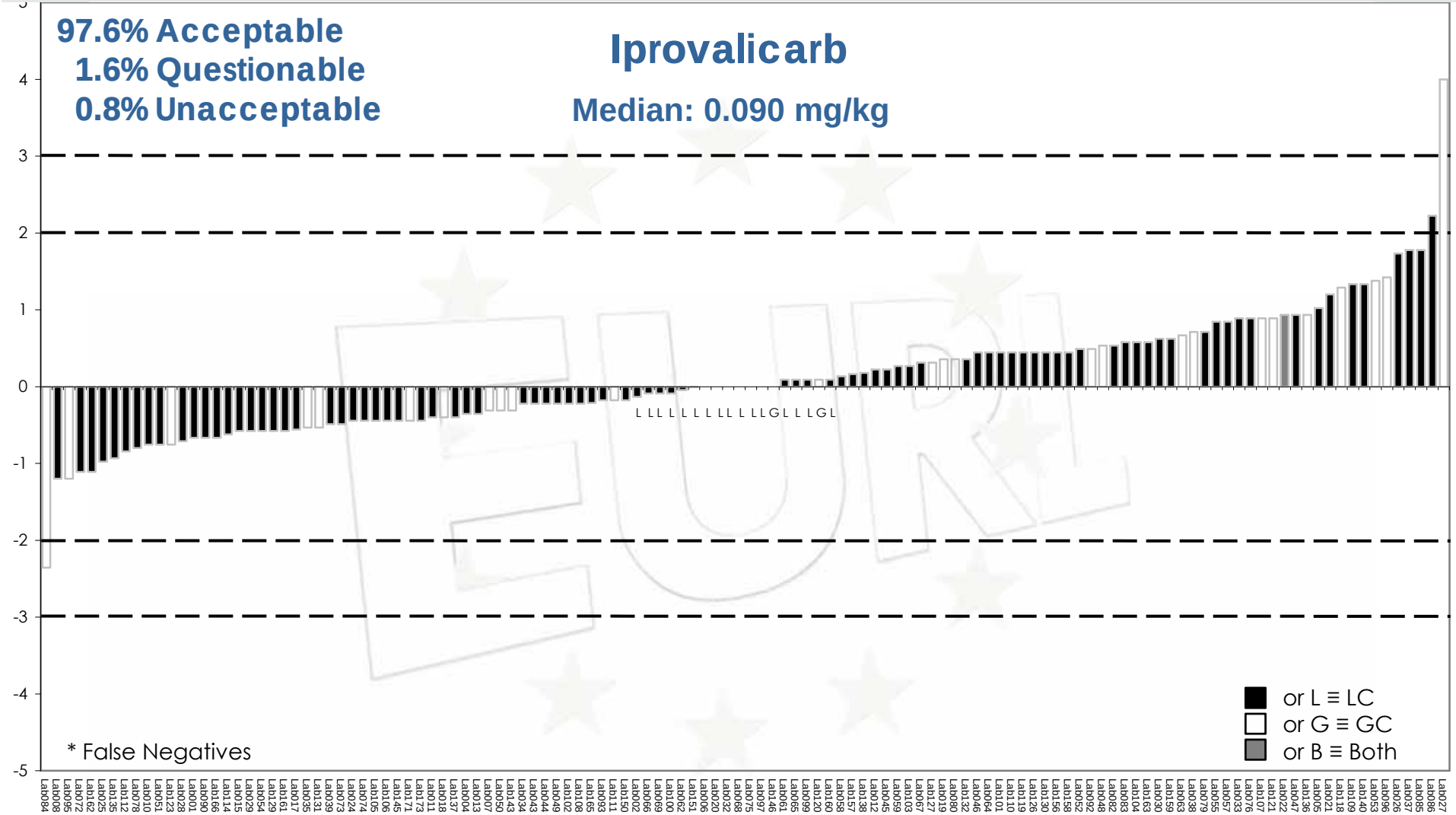

89% Acceptable
6% Questionable
5% Unacceptable
Cypermethrin
Median: 0.100 mg/kg
GGGGL LGGGGG
******
* False Negatives
or L ≡ LC
or G ≡ GC
or B ≡ Both

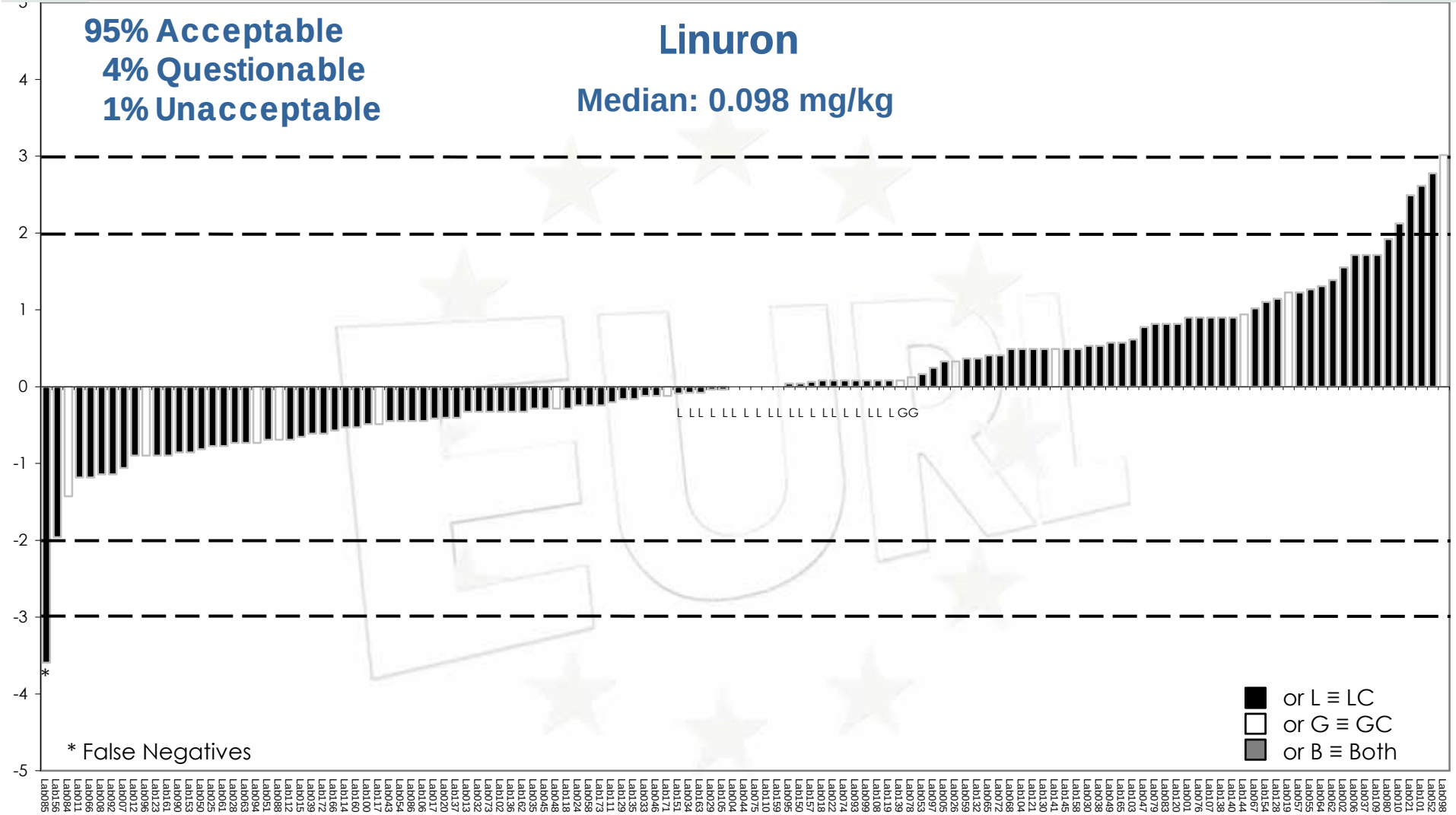

95% Acceptable
3% Questionable
2% Unacceptable
Diazinon
Median: 0.195 mg/kg
GGGLGGGGLG
* False Negatives
or L ≡ LC
or G ≡ GC
or B ≡ Both

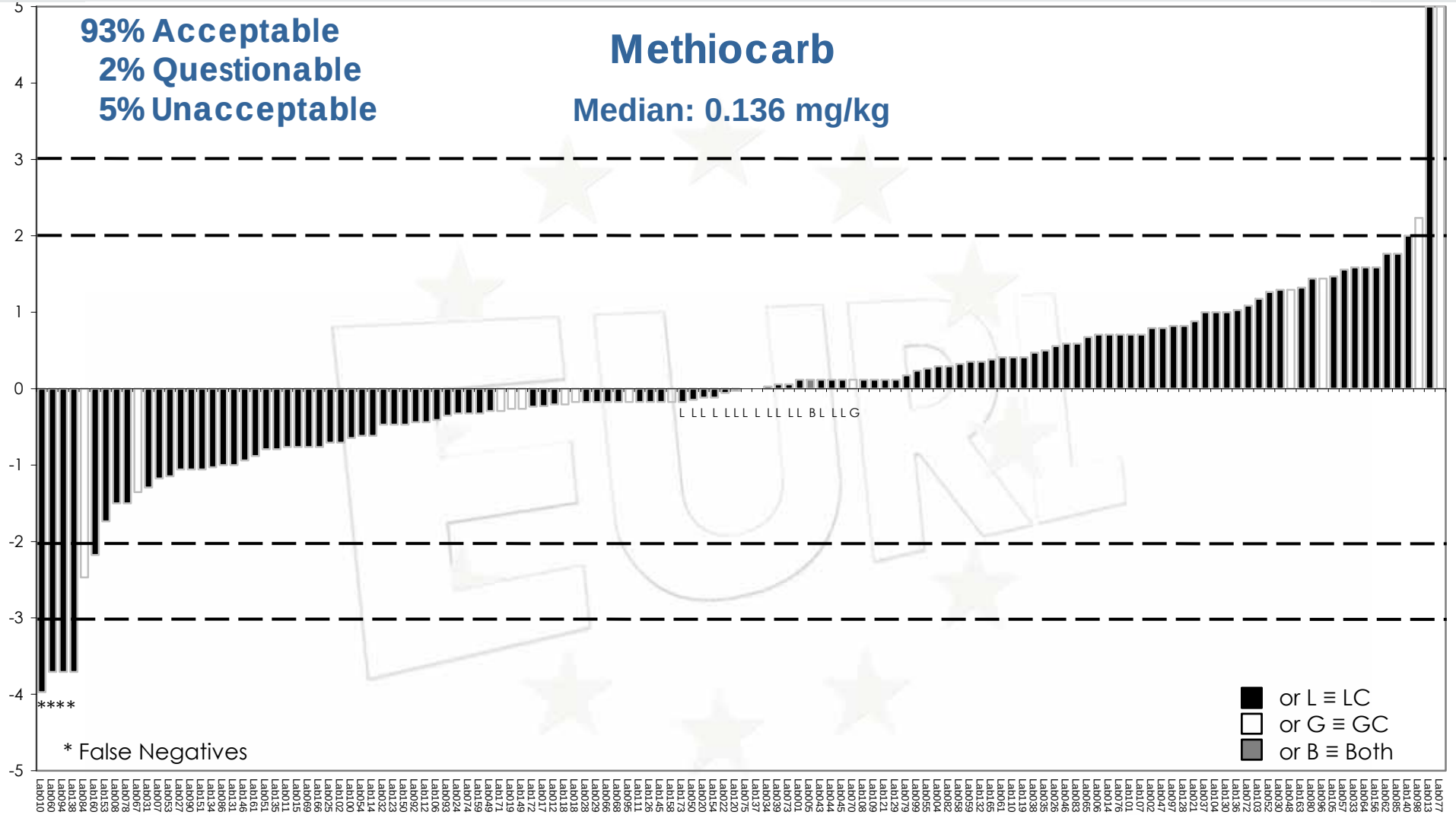

96% Acceptable
4% Questionable
0% Unacceptable
Fluopicolide
Median: 0.099 mg/kg
4
3
2
1
0
-1
-2
-3
-4
-5
G G L L G L G G G G L G L L G L L
* False Negatives
or L ≡ LC
or G ≡ GC
or B ≡ Both
Lab084 Lab078 Lab090 Lab137 Lab013 Lab039 Lab051 Lab050 Lab166 Lab161 Lab015 Lab173 Lab002 Lab123 Lab112 Lab129 Lab008 Lab018 Lab100 Lab105 Lab025 Lab061 Lab022 Lab029 Lab106 Lab011 Lab017 Lab099 Lab118 Lab150 Lab024 Lab068 Lab046 Lab093 Lab103 Lab042 Lab066 Lab120 Lab007 Lab012 Lab044 Lab074 Lab108 Lab136 Lab143 Lab163 Lab038 Lab067 Lab028 Lab035 Lab064 Lab086 Lab111 Lab119 Lab121 Lab020 Lab075 Lab097 Lab034 Lab052 Lab102 Lab030 Lab079 Lab165 Lab049 Lab059 Lab149 Lab171 Lab043 Lab045 Lab156 Lab065 Lab083 Lab131 Lab132 Lab054 Lab073 Lab005 Lab048 Lab055 Lab047 Lab104 Lab004 Lab092 Lab107 Lab062 Lab057 Lab037 Lab145 Lab109 Lab138 Lab080 Lab010 Lab026 Lab110

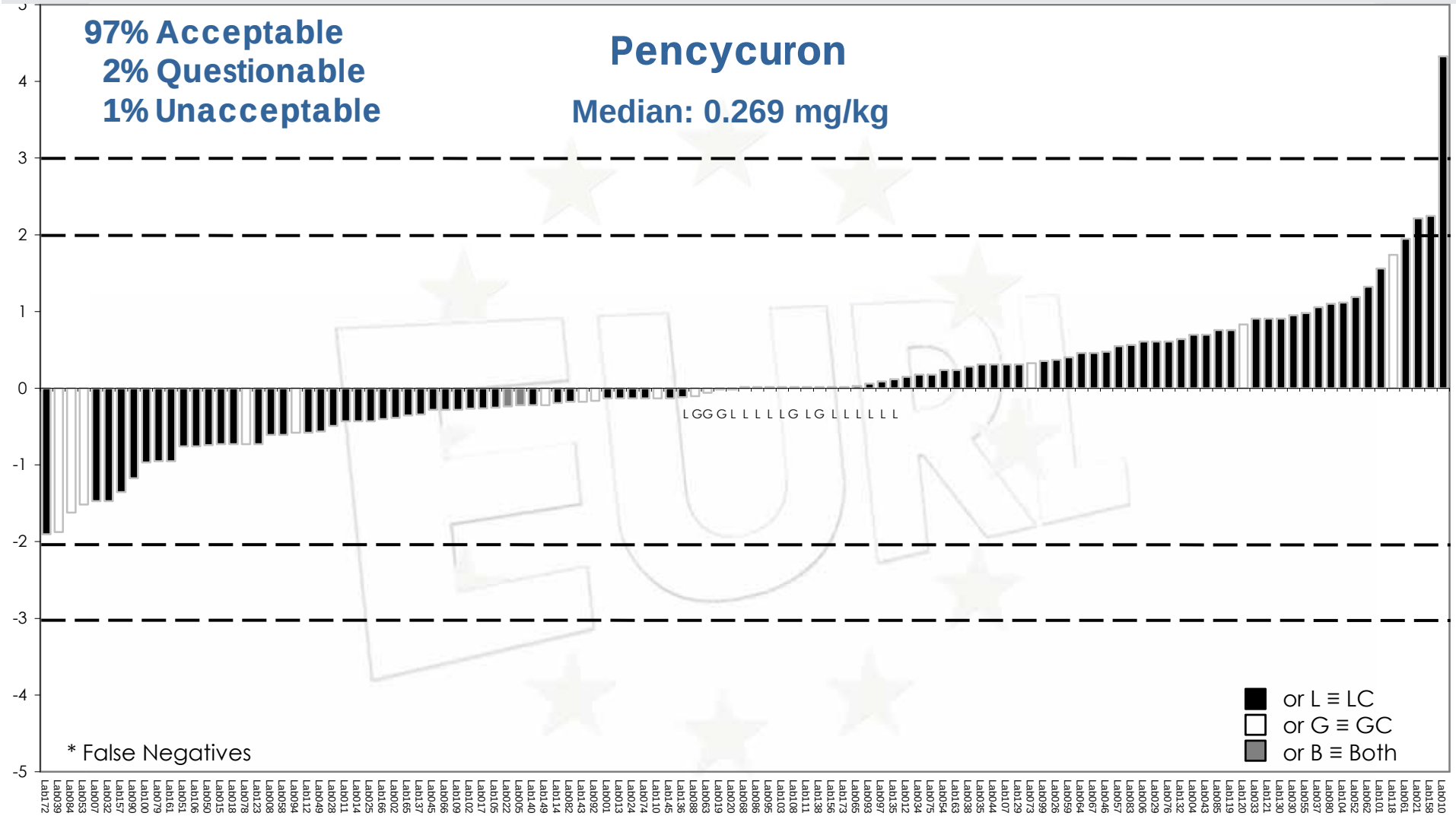

96% Acceptable
2% Questionable
2% Unacceptable
Flutolanil
Median: 0.410 mg/kg
5
4
3
2
1
0
-1
-2
-3
-4
-5
G L G G G L G L L L L L L G
* False Negatives
or L ≡ LC
or G ≡ GC
or B ≡ Both
Lab083 Lab084 Lab123 Lab090 Lab039 Lab161 Lab165 Lab072 Lab008 Lab015 Lab025 Lab137 Lab051 Lab096 Lab166 Lab012 Lab001 Lab074 Lab086 Lab108 Lab050 Lab112 Lab054 Lab018 Lab022 Lab105 Lab062 Lab094 Lab099 Lab011 Lab052 Lab118 Lab024 Lab028 Lab013 Lab002 Lab106 Lab030 Lab100 Lab017 Lab068 Lab067 Lab173 Lab004 Lab035 Lab103 Lab078 Lab093 Lab104 Lab029 Lab061 Lab066 Lab129 Lab044 Lab111 Lab121 Lab042 Lab120 Lab102 Lab007 Lab058 Lab059 Lab109 Lab138 Lab145 Lab020 Lab021 Lab034 Lab097 Lab075 Lab149 Lab064 Lab119 Lab171 Lab132 Lab107 Lab005 Lab110 Lab065 Lab057 Lab043 Lab046 Lab049 Lab006 Lab095 Lab156 Lab143 Lab079 Lab038 Lab092 Lab073 Lab055 Lab136 Lab033 Lab163 Lab026 Lab080 Lab037 Lab045 Lab010

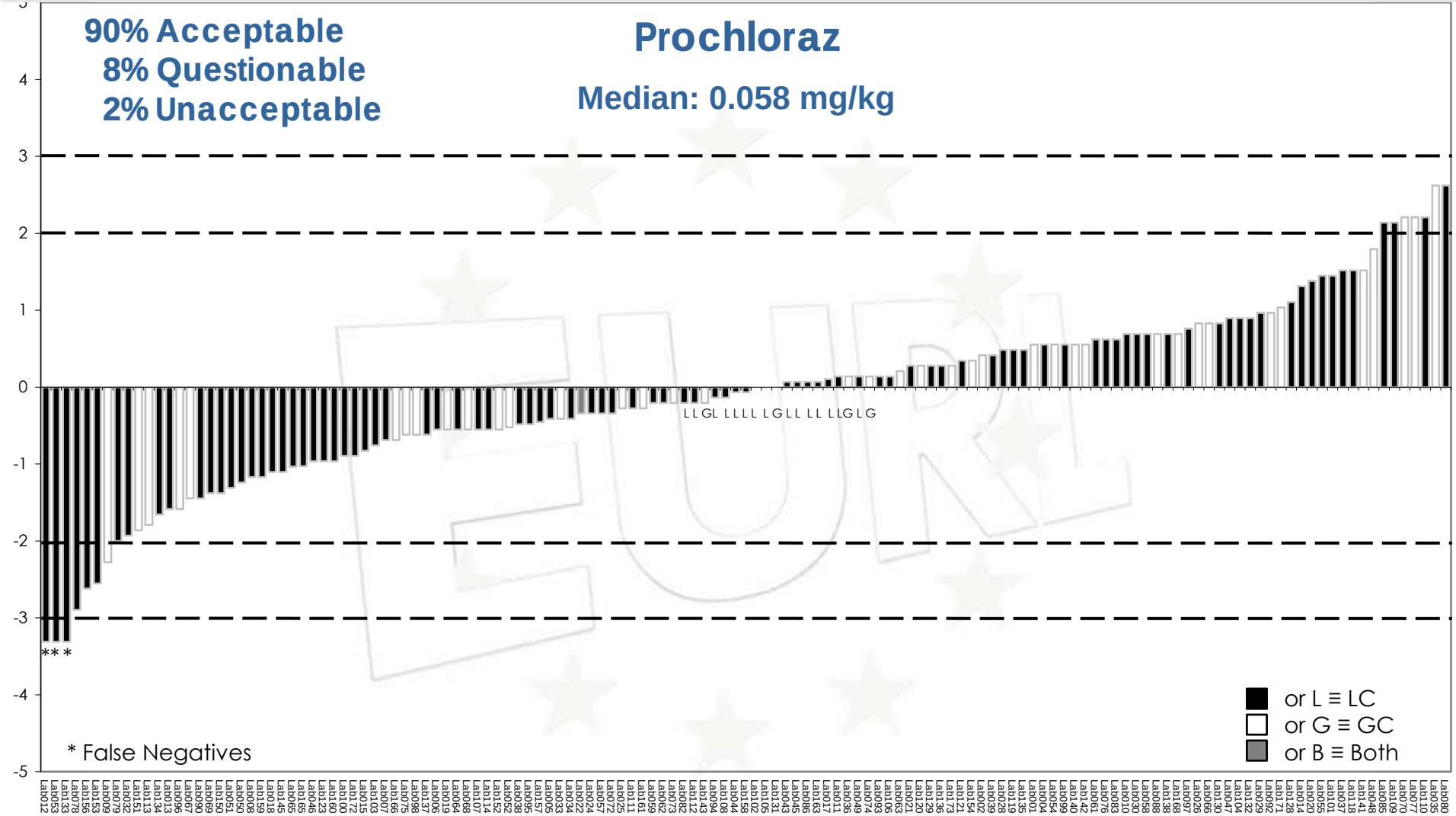

96% Acceptable
2% Questionable
2% Unacceptable
Fosthiazate
Median: 0.080 mg/kg
5
4
3
2
1
0
-1
-2
-3
-4
-5
G G G G G L L L G L L L L G L L L L G L
*
* False Negatives
or L ≡ LC
or G ≡ GC
or B ≡ Both
Lab058 Lab053 Lab156 Lab002 Lab082 Lab025 Lab029 Lab008 Lab106 Lab130 Lab046 Lab100 Lab129 Lab050 Lab051 Lab028 Lab105 Lab011 Lab062 Lab001 Lab035 Lab090 Lab112 Lab086 Lab012 Lab049 Lab015 Lab054 Lab166 Lab007 Lab102 Lab123 Lab061 Lab173 Lab024 Lab043 Lab068 Lab137 Lab018 Lab055 Lab065 Lab079 Lab093 Lab132 Lab034 Lab066 Lab172 Lab009 Lab075 Lab097 Lab013 Lab067 Lab074 Lab103 Lab111 Lab171 Lab020 Lab101 Lab108 Lab059 Lab080 Lab145 Lab165 Lab039 Lab095 Lab017 Lab033 Lab083 Lab004 Lab044 Lab057 Lab136 Lab119 Lab121 Lab022 Lab076 Lab078 Lab099 Lab006 Lab104 Lab120 Lab161 Lab163 Lab005 Lab030 Lab073 Lab038 Lab052 Lab026 Lab109 Lab064 Lab107 Lab092 Lab037 Lab110 Lab021 Lab118 Lab010 Lab045 Lab077 Lab084 Lab027

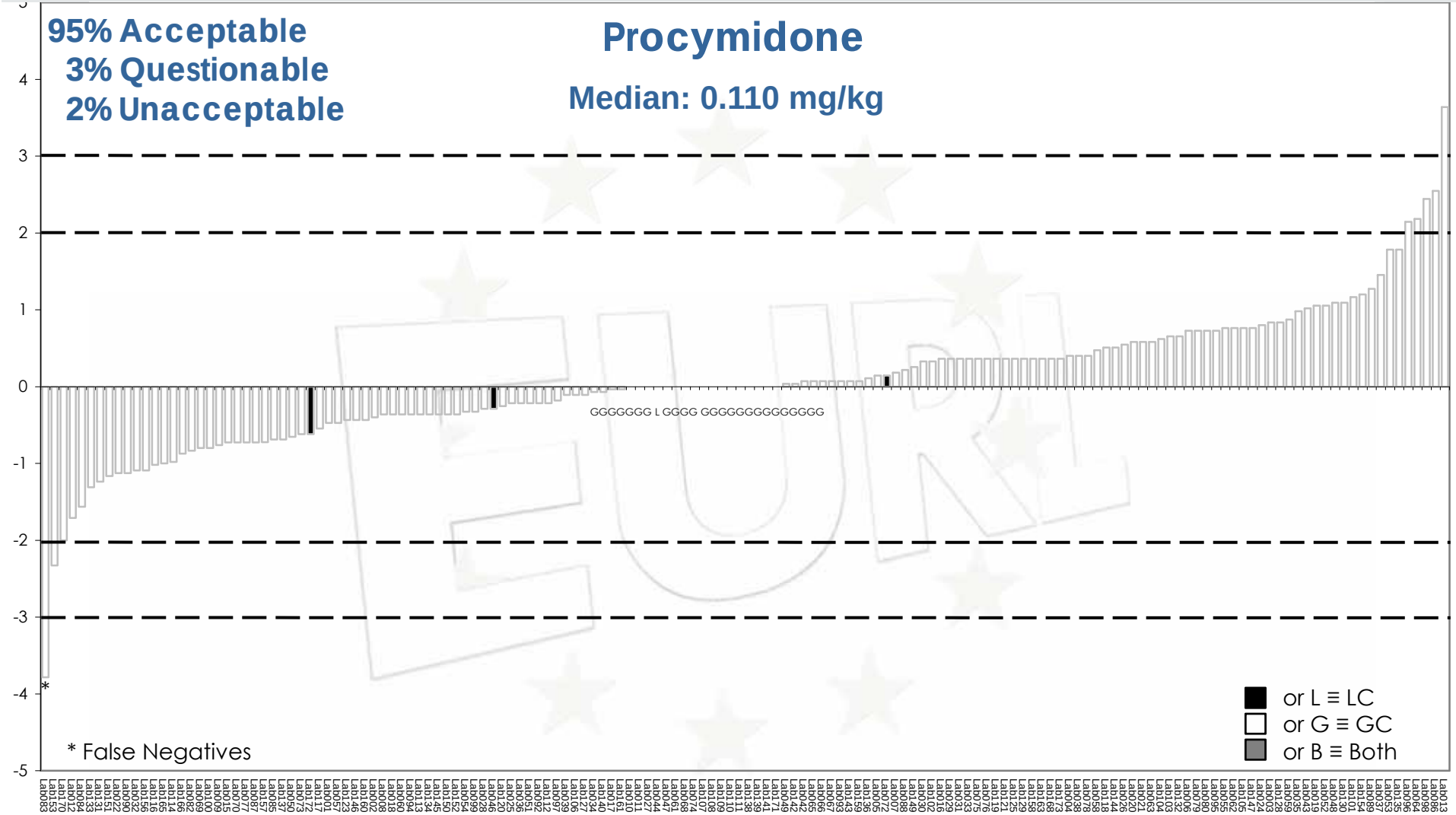

97.6% Acceptable
1.6% Questionable
0.8% Unacceptable
Iprovalicarb
Median: 0.090 mg/kg
4
3
2
1
0
-1
-2
-3
-4
-5
L L L L L L L LL L LLGL L L GL
* False Negatives
or L ≡ LC
or G ≡ GC
or B ≡ Both

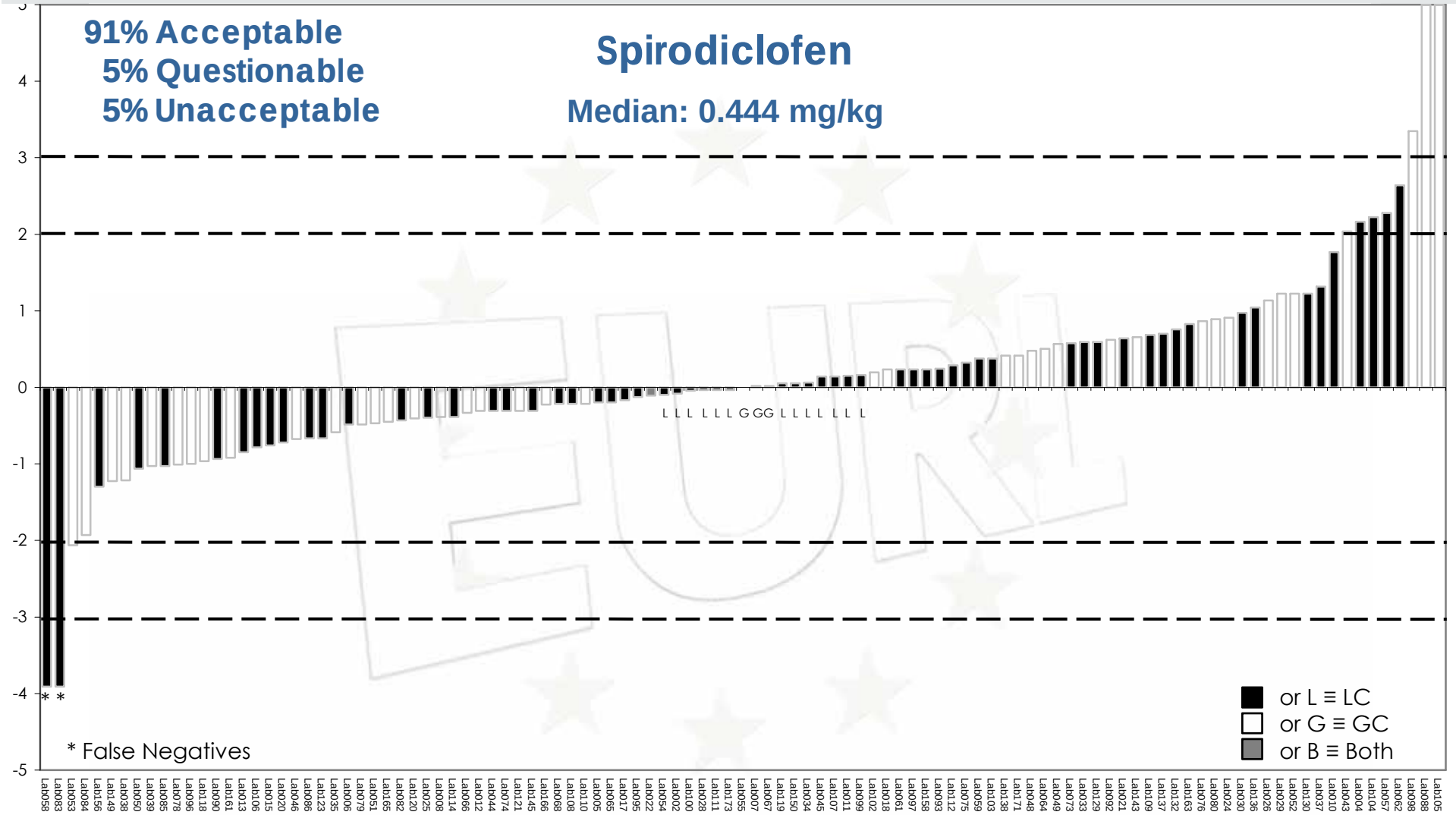

95% Acceptable
4% Questionable
1% Unacceptable
Linuron
Median: 0.098 mg/kg
4
3
2
1
0
-1
-2
-3
-4
-5
L LL L LL L L LL LL L LL L L LL L GG
*
* False Negatives
or L ≡ LC
or G ≡ GC
or B ≡ Both

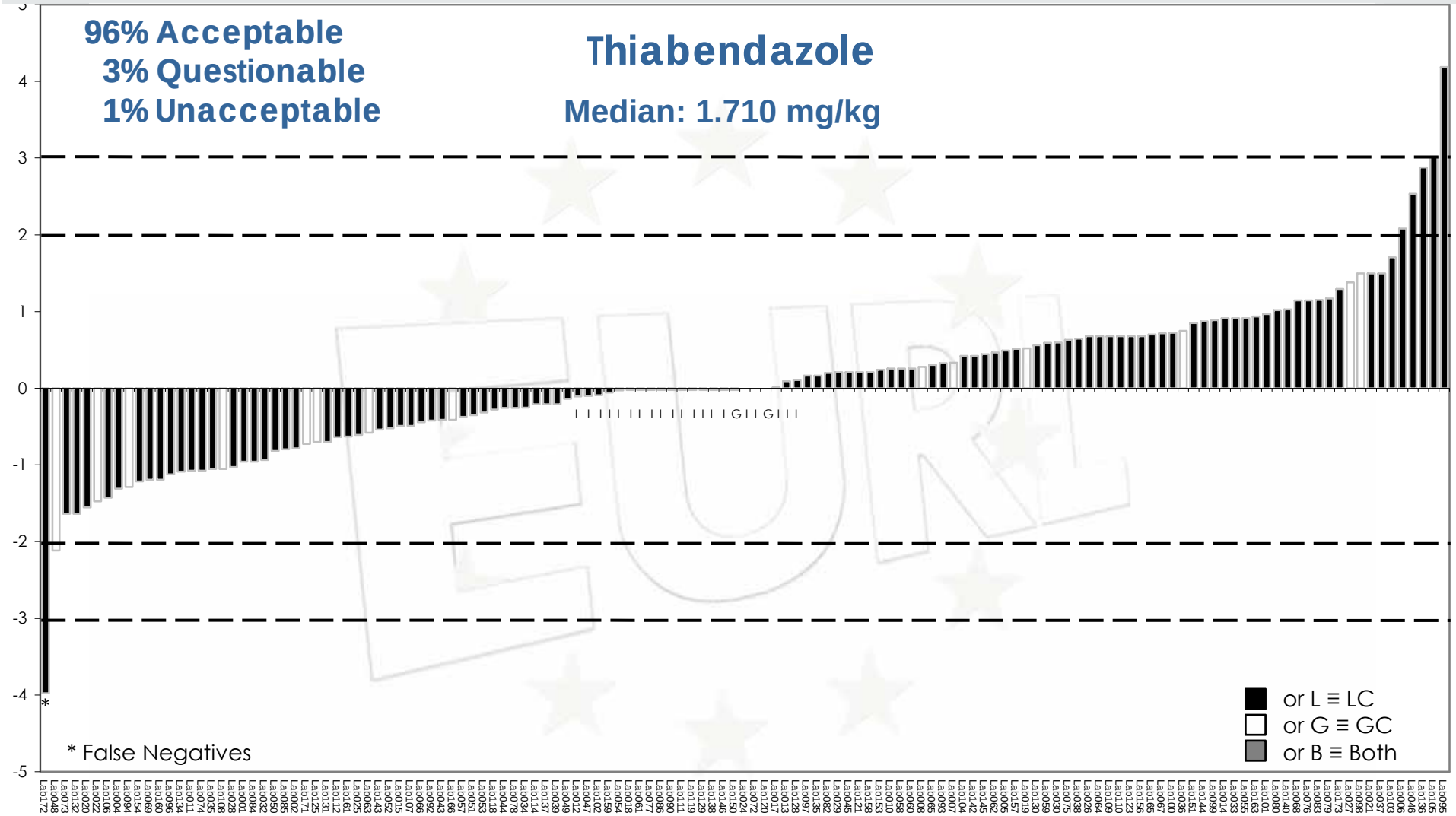

93% Acceptable
2% Questionable
5% Unacceptable
Methiocarb
Median: 0.136 mg/kg
5
4
3
2
1
0
-1
-2
-3
-4
-5
L LL L LLL L LL LL BL LLG
****
* False Negatives
or L ≡ LC
or G ≡ GC
or B ≡ Both

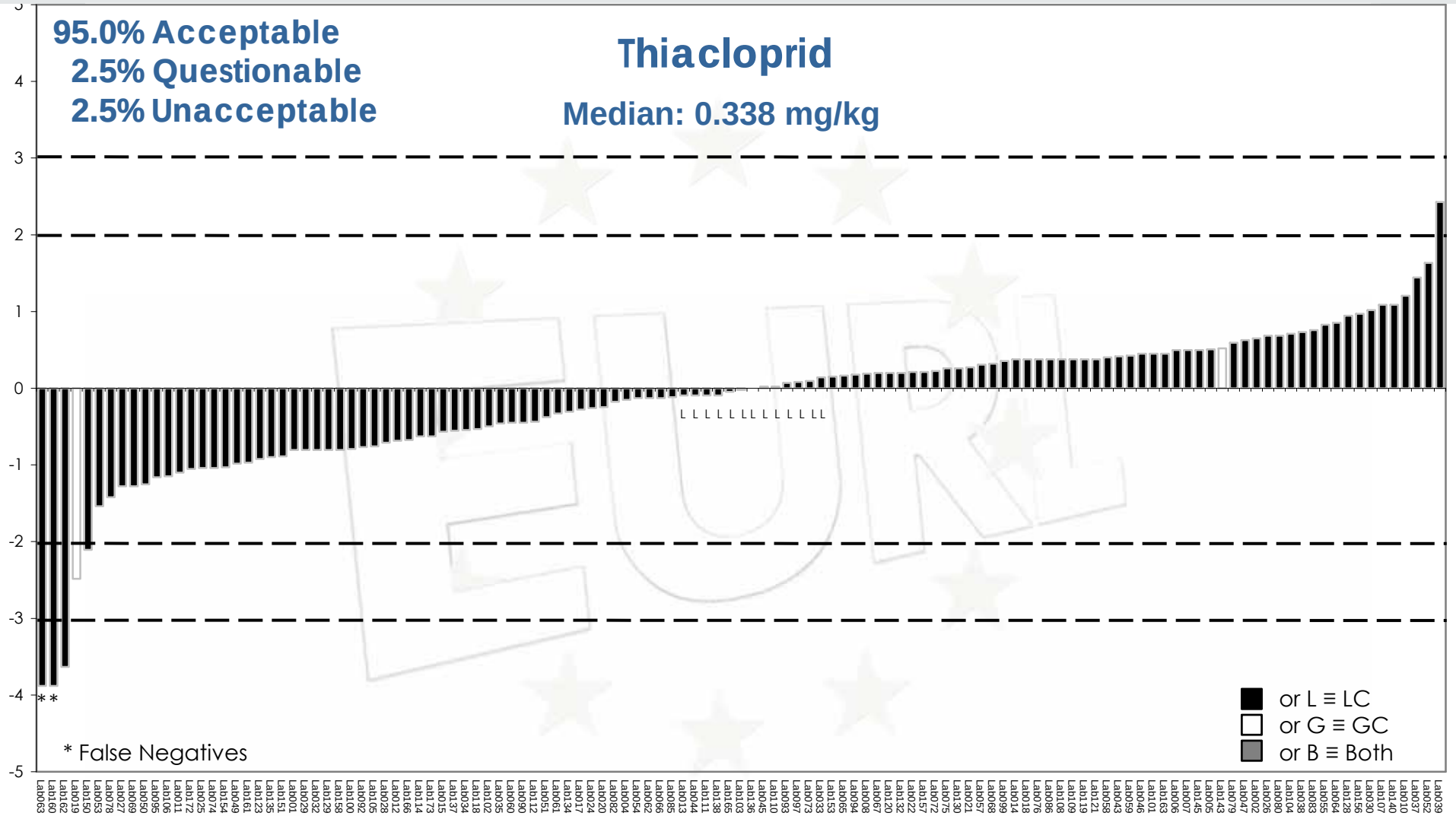

97% Acceptable
2% Questionable
1% Unacceptable
Pencycuron
Median: 0.269 mg/kg
4
3
2
1
0
-1
-2
-3
-4
-5
LGGGLLLLLGLGLLLLLL
* False Negatives
or L ≡ LC
or G ≡ GC
or B ≡ Both


90% Acceptable
8% Questionable
2% Unacceptable
Prochloraz
Median: 0.058 mg/kg
4
3
2
1
0
-1
-2
-3
-4
-5
L L GL L L L L L G L L L L L L G L G
* * *
* False Negatives
or L ≡ LC
or G ≡ GC
or B ≡ Both


95% Acceptable
3% Questionable
2% Unacceptable
Procymidone
Median: 0.110 mg/kg
GGGGGGG L GGGG GGGGGGGGGGGGGG
* False Negatives
or L ≡ LC
or G ≡ GC
or B ≡ Both


91% Acceptable
5% Questionable
5% Unacceptable
Spirodiclofen
Median: 0.444 mg/kg
L L L L L L L G G G L L L L L L L L
* *
* False Negatives
or L ≡ LC
or G ≡ GC
or B ≡ Both
5
4
3
2
1
0
-1
-2
-3
-4
-5
Lab058 Lab083 Lab053 Lab084 Lab156 Lab149 Lab038 Lab050 Lab039 Lab085 Lab078 Lab096 Lab118 Lab090 Lab161 Lab013 Lab106 Lab015 Lab020 Lab046 Lab086 Lab123 Lab035 Lab006 Lab079 Lab051 Lab165 Lab082 Lab120 Lab025 Lab008 Lab114 Lab066 Lab012 Lab044 Lab074 Lab121 Lab145 Lab166 Lab068 Lab108 Lab110 Lab005 Lab065 Lab017 Lab095 Lab022 Lab054 Lab002 Lab100 Lab028 Lab111 Lab173 Lab055 Lab007 Lab067 Lab119 Lab150 Lab034 Lab045 Lab107 Lab011 Lab099 Lab102 Lab018 Lab061 Lab097 Lab158 Lab093 Lab112 Lab075 Lab059 Lab103 Lab138 Lab171 Lab048 Lab064 Lab049 Lab073 Lab033 Lab129 Lab092 Lab021 Lab143 Lab109 Lab137 Lab132 Lab163 Lab076 Lab080 Lab024 Lab030 Lab136 Lab026 Lab029 Lab052 Lab130 Lab037 Lab010 Lab043 Lab004 Lab104 Lab057 Lab062 Lab098 Lab088 Lab105


96% Acceptable
3% Questionable
1% Unacceptable
Thiabendazole
Median: 1.710 mg/kg
4
3
2
1
0
-1
-2
-3
-4
-5
L L LLL LL LL LL LLL LGLLGLLL
*
* False Negatives
or L ≡ LC
or G ≡ GC
or B ≡ Both


95.0% Acceptable
2.5% Questionable
2.5% Unacceptable
Thiacloprid
Median: 0.338 mg/kg
5
4
3
2
1
0
-1
-2
-3
-4
-5
**
* False Negatives
or L ≡ LC
or G ≡ GC
or B ≡ Both

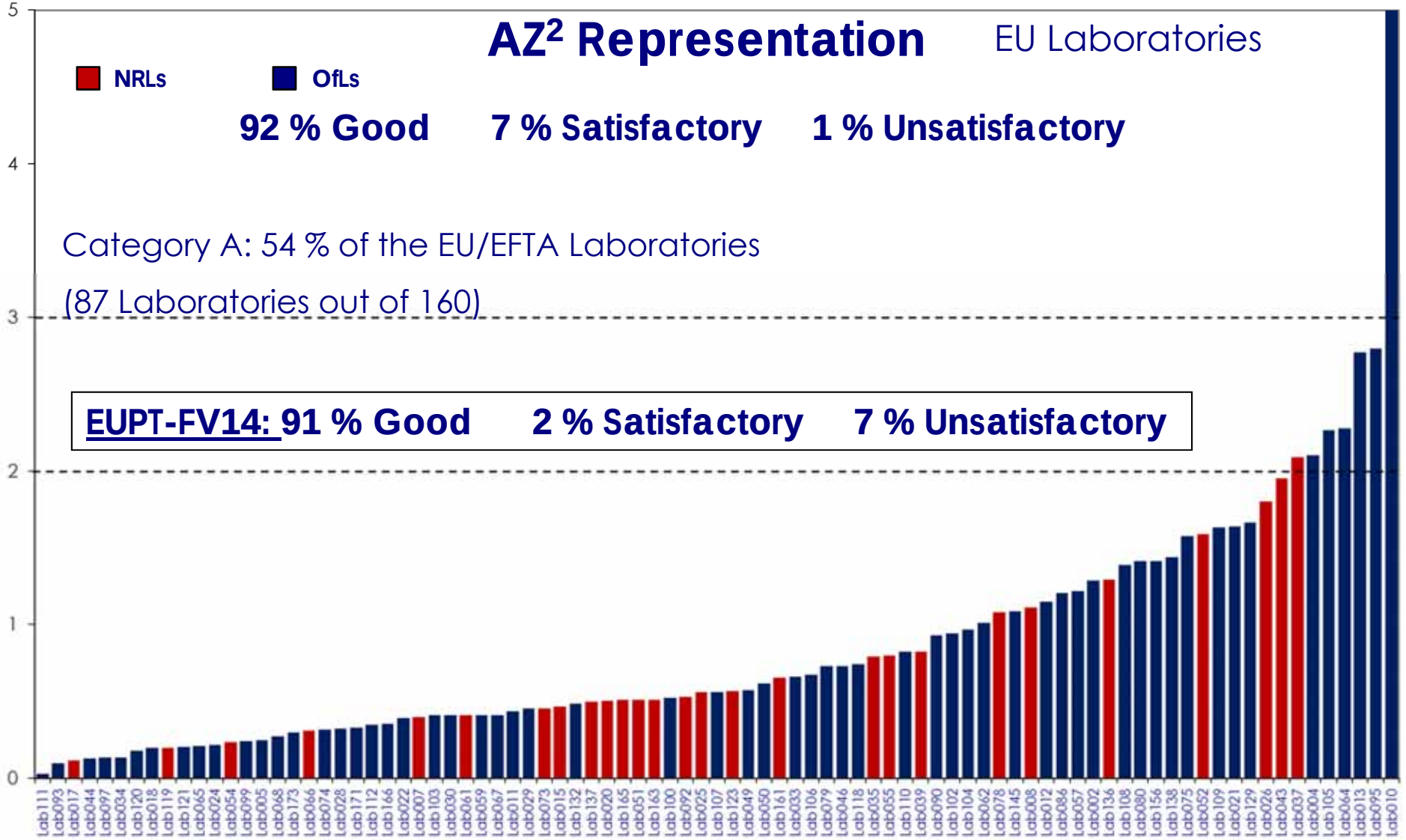
Combined z-Scores

Average of Squared z-Scores

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

AZ^2	≤ 2	Good
$2 <$ AZ^2	≤ 3	Satisfactory
AZ^2	> 3	Unsatisfactory

AZ² Representation EU Laboratories



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)
Lab038	Captan	0.131	GC-MSD (EI)	0.01	0,01
Lab060	Dimethomorph	0.110	LC-MS/MS (QQQ) (ESI+)	0.01	0.01
Lab077	Carbendazim (sum of benomyl and carbendazim expressed as carbendazim)	0.040	HPLC-FD Confirmation: GC-MS/MS (QQQ) (EI+)	0.01	0.01
Lab114	Methiocarb sulfone	0.612	LC-MS/MS (QQQ) (ESI+)	0.01	0.01
Lab128	Fludioxonil	0.123	LC-MS/MS (QQQ)	0.01	0.01
Lab160	Tebuconazole	0.011	LC-MS/MS (QQQ) (ESI+)	0.01	0.01

False Positives

GC-MS or GC-MS/MS

Captan

Carbendazim

LC-MS/MS or LC-FD

Carbendazim

Dimethomorph

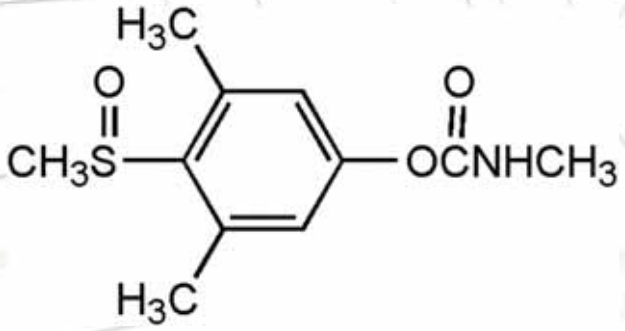
Fludioxonil

Methiocarb sulfone

Tebuconazole

Other detected pesticides

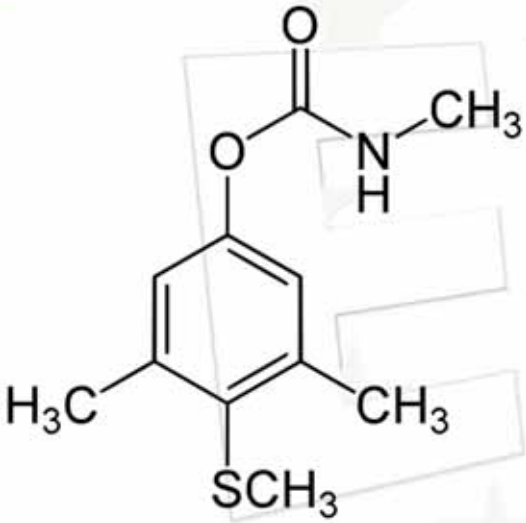
Metabolites



Methiocarb sulfoxide

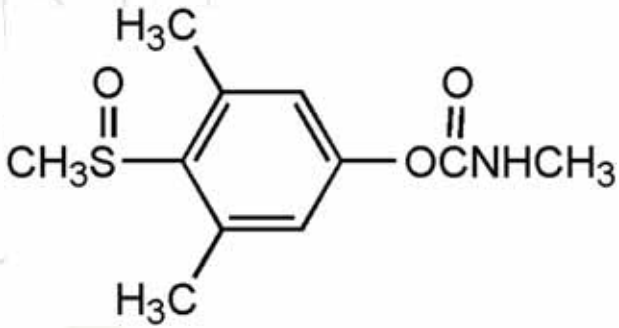
Other detected pesticides

Spiked with methiocarb



Methiocarb

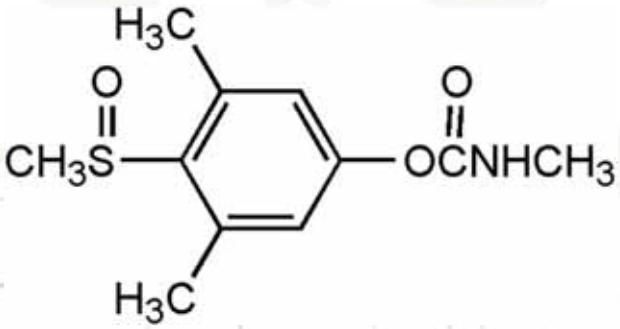
0.136 mg/kg



Methiocarb sulfoxide

0.013 mg/kg

Other detected pesticides



Methiocarb sulfoxide

0.013 mg/kg

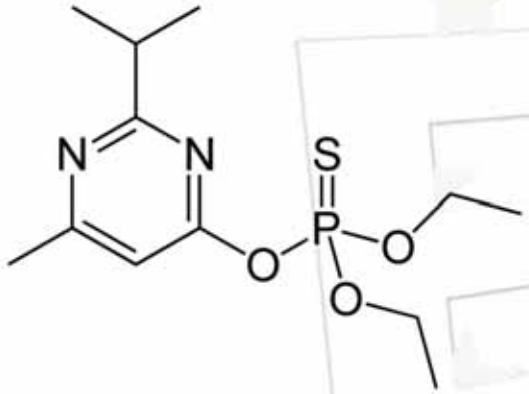
Not used for the evaluation of the laboratories for statistical reasons

Other detected pesticides

Impurities of commercial formulations

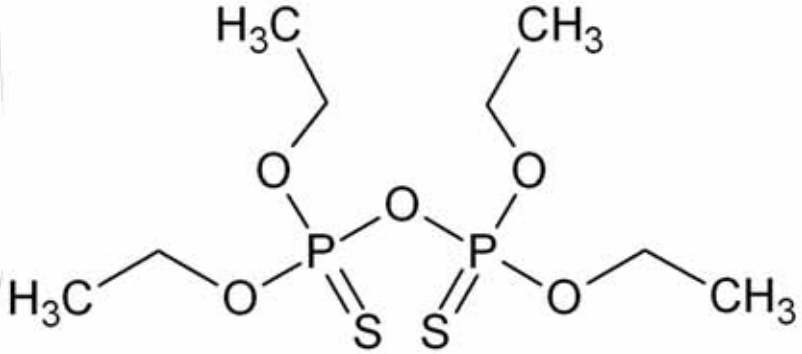
Other detected pesticides

Spiked with diazinon



Diazinon

0.195 mg/kg

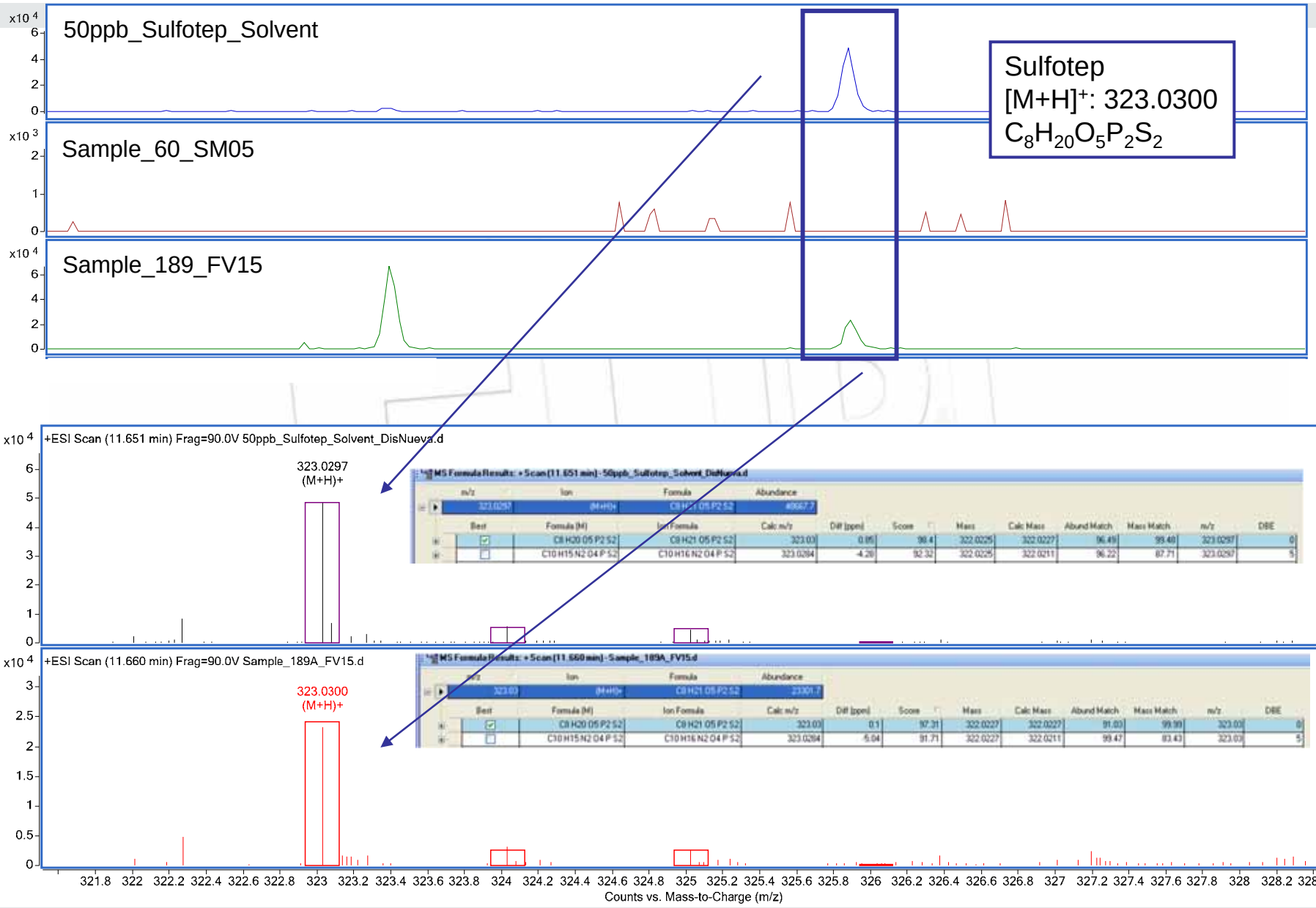


Sulfotep

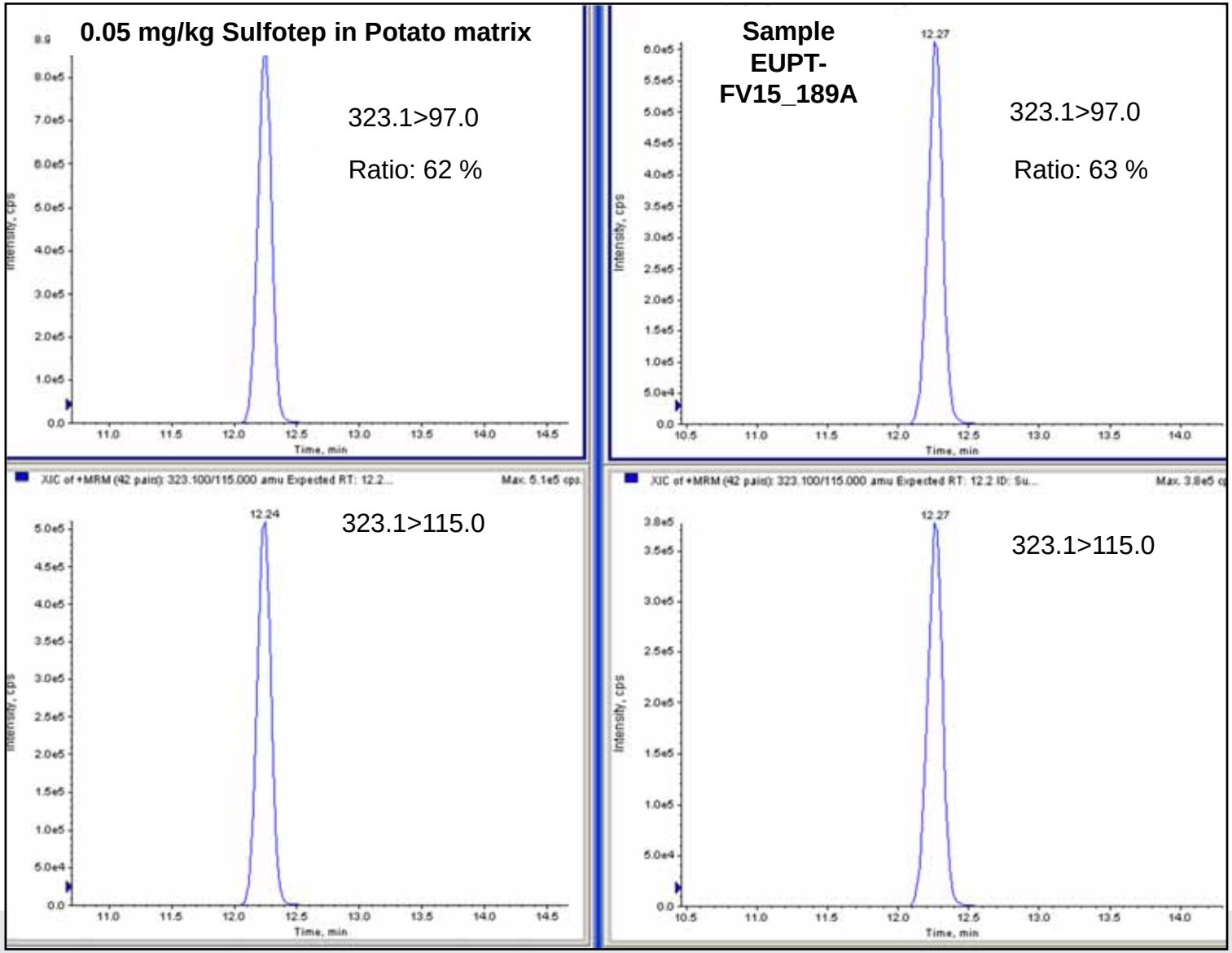
Aprox. 0.040 mg/kg

(NOT included in the target list)

LC-QTOF-MS


50ppb_Sulfotep_Solvent
Sample_60_SM05
Sample_189_FV15
Sulfotep
[M+H]+: 323.0300
C8H20O5P2S2
+ESI Scan (11.651 min) Frag=90.0V 50ppb_Sulfotep_Solvent_DisNueva.d
323.0297
(M+H)+
+ESI Scan (11.660 min) Frag=90.0V Sample_189A_FV15.d
323.0300
(M+H)+
Counts vs. Mass-to-Charge (m/z)

LC-QQQ-MS/MS


0.05 mg/kg Sulfotep in Potato matrix
323.1>97.0
Ratio: 62 %
Sample EUPT-FV15_189A
323.1>97.0
Ratio: 63 %
323.1>115.0
323.1>115.0
Intensity, cps
Time, min

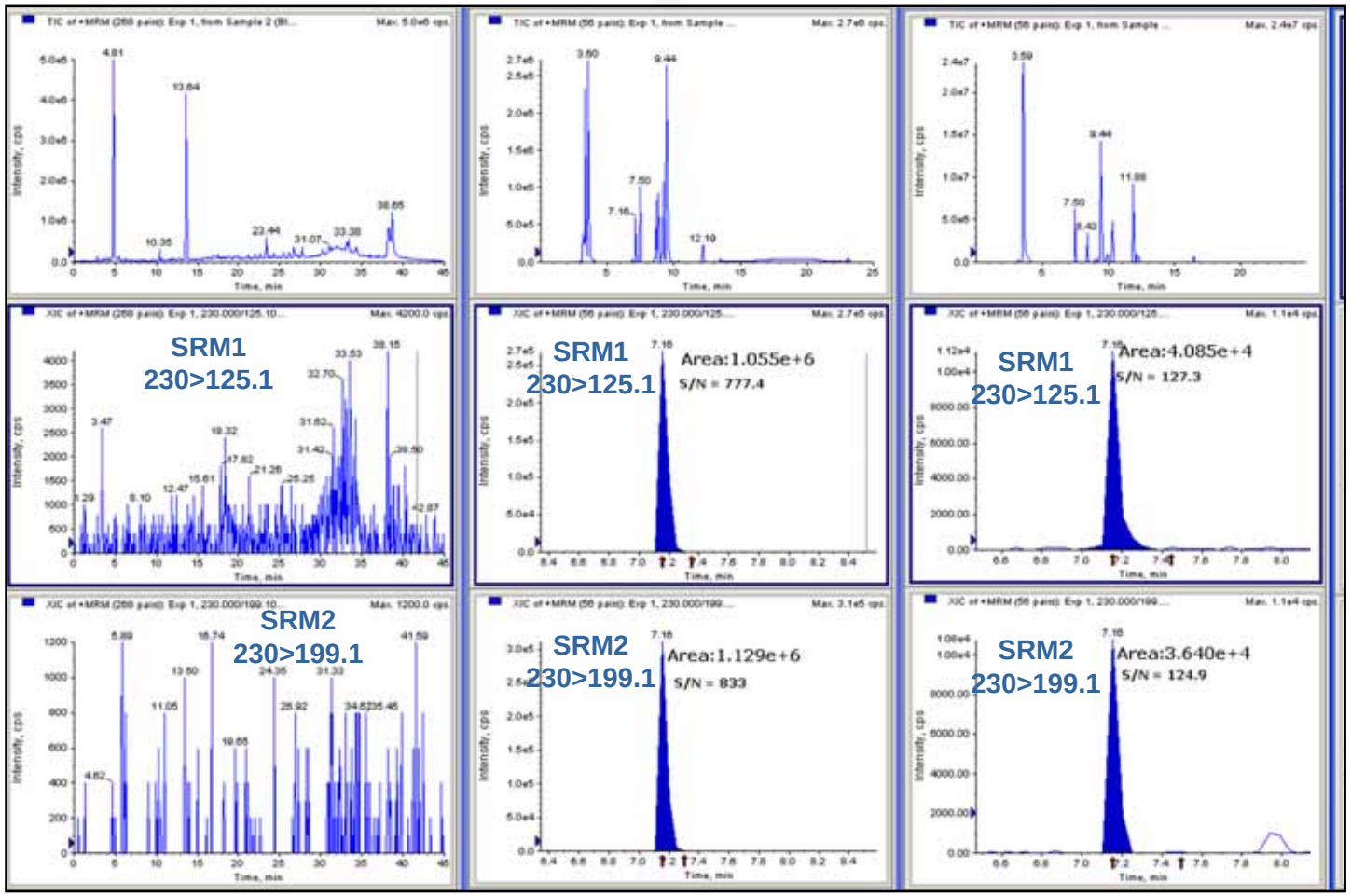
Other detected pesticides

Contamination of comercial formulations

DIMETHOATE

(Found in the sample at approx. 3 µg/kg)

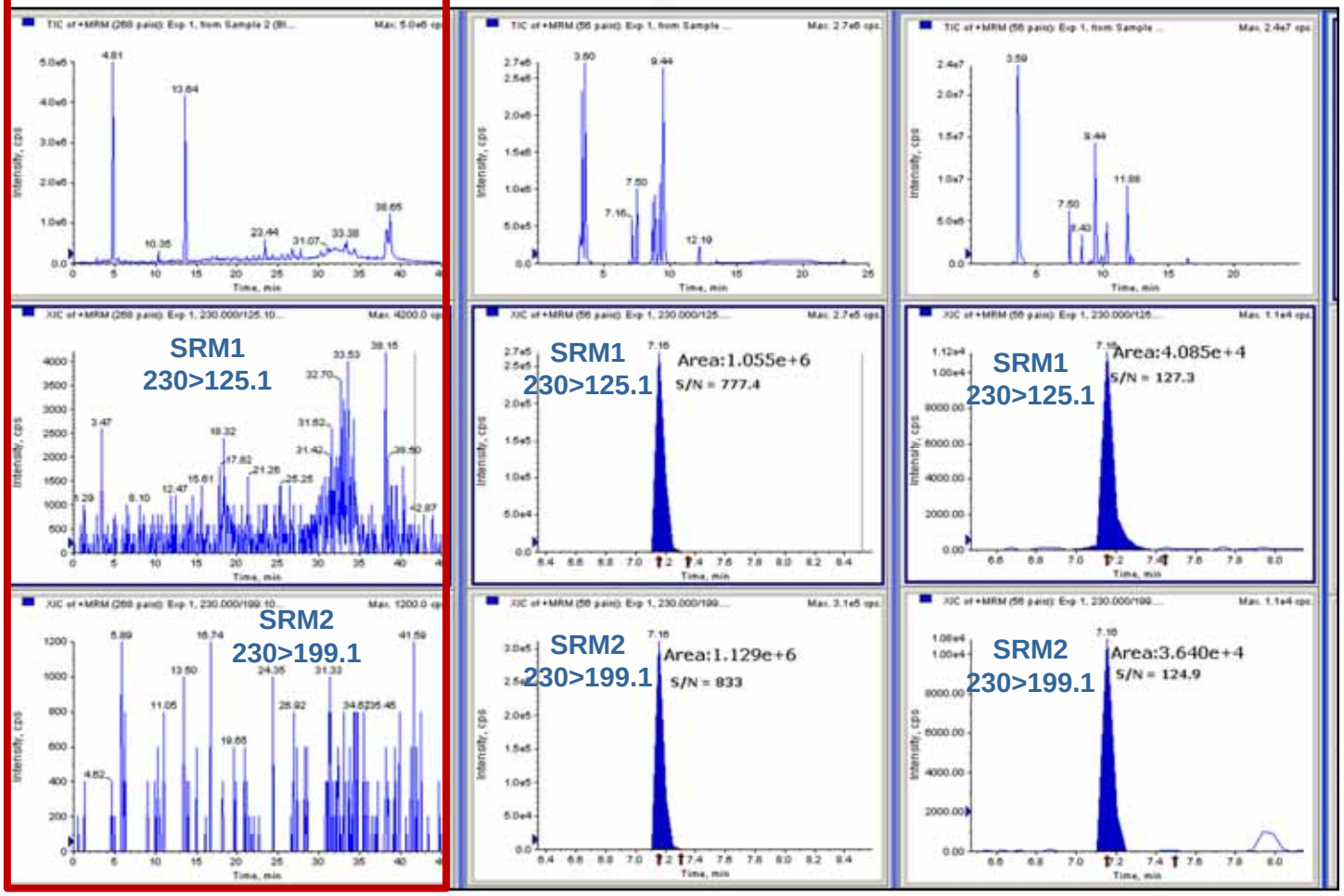
BLANK POTATO **Std. 10 µg/kg POTATO** **SAMPLE 79A FV15**



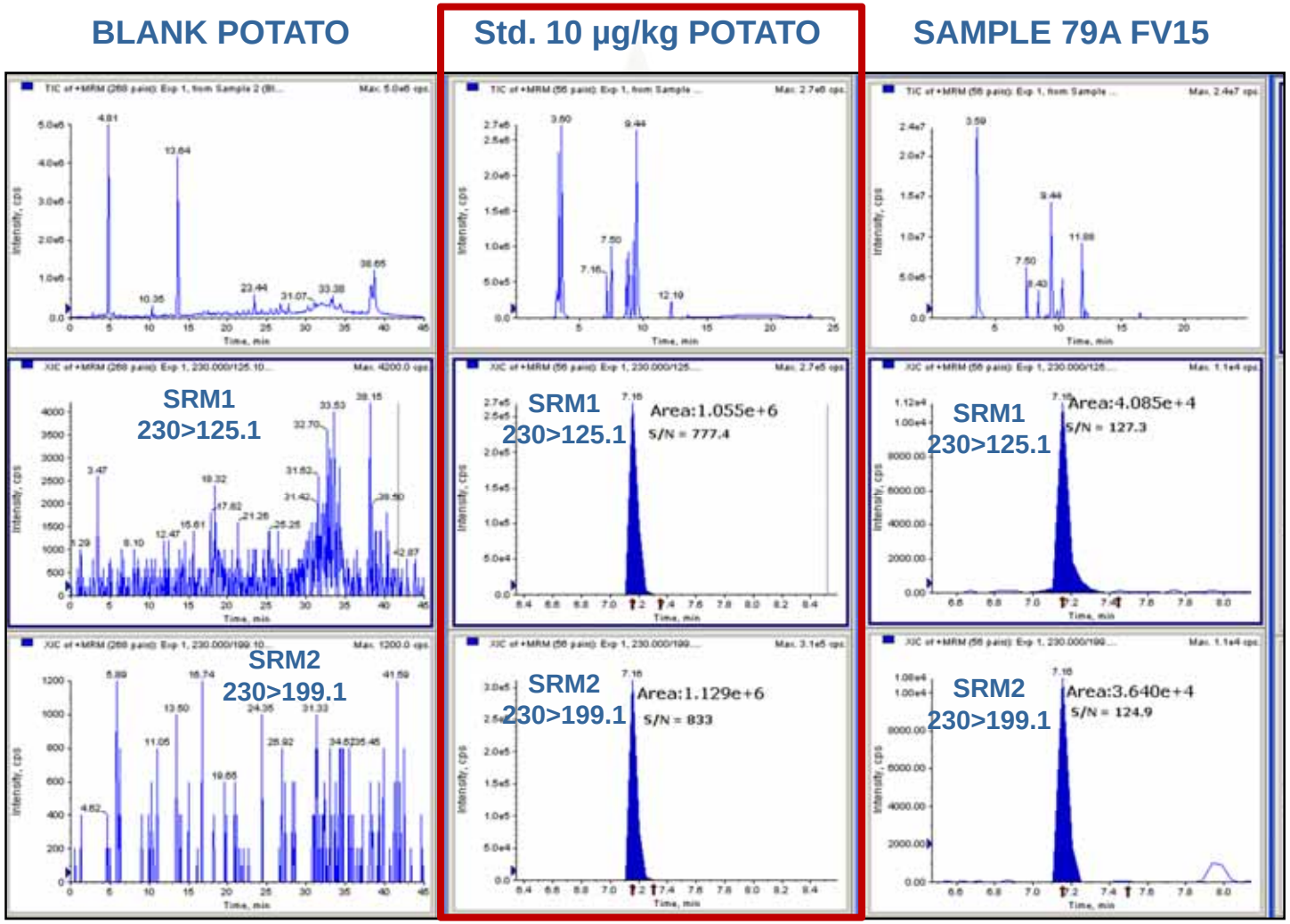
DIMETHOATE

(Found in the sample at approx. 3 µg/kg)

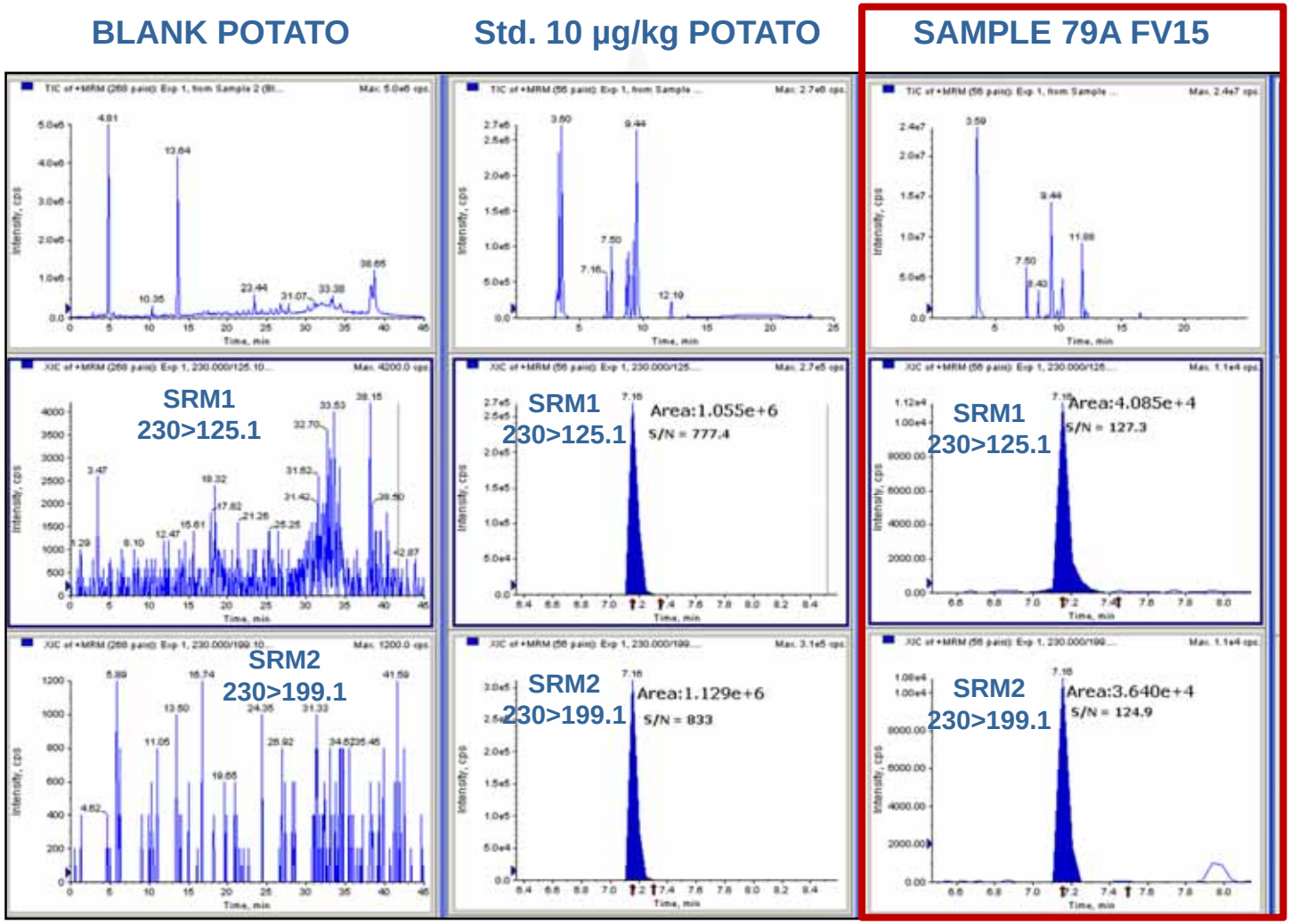
BLANK POTATO	Std. 10 µg/kg POTATO	SAMPLE 79A FV15



DIMETHOATE
(Found in the sample at approx. 3 µg/kg)

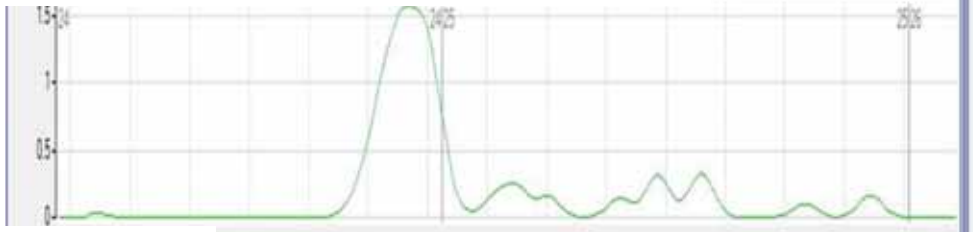


DIMETHOATE
(Found in the sample at approx. 3 µg/kg)

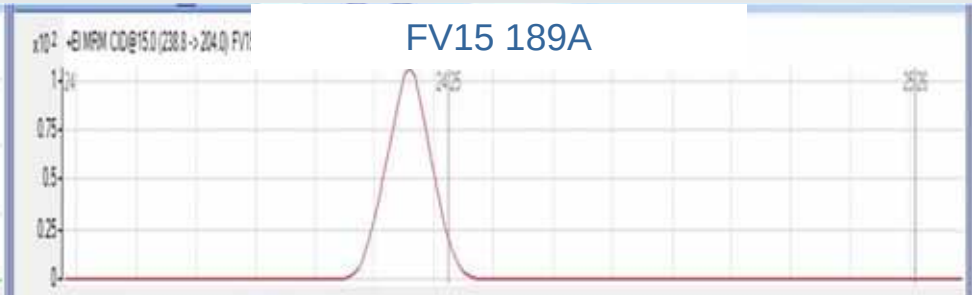


Endosulfan Alpha (concentration < 10 µg/kg)

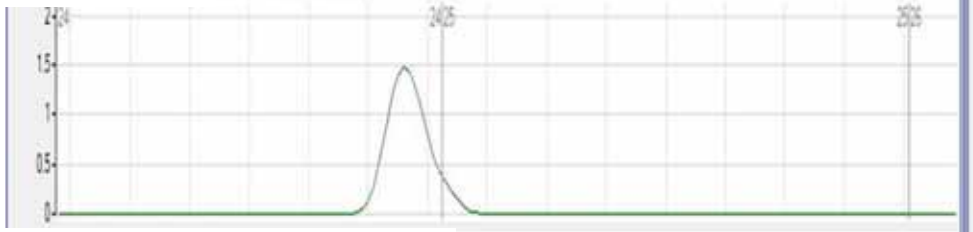
238.8>204 Std. 5 µg/kg Potato

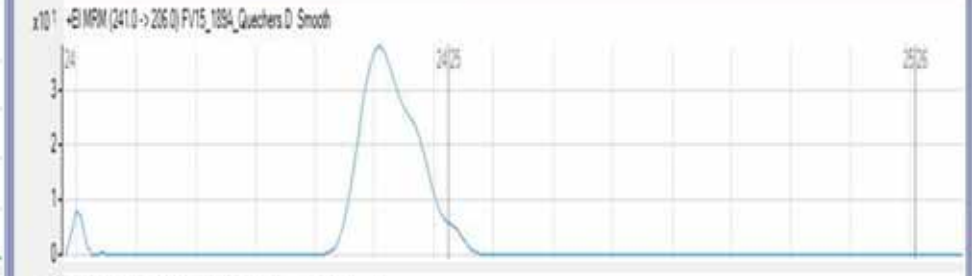


FV15 189A

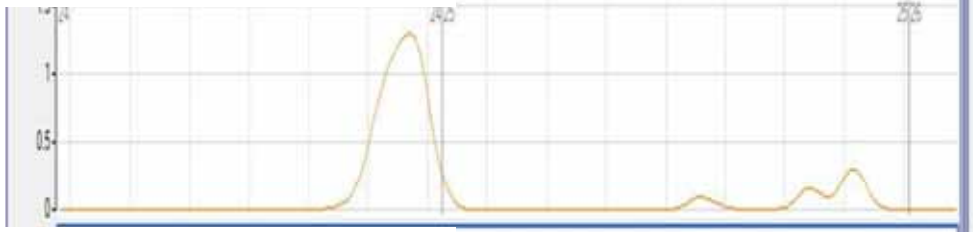


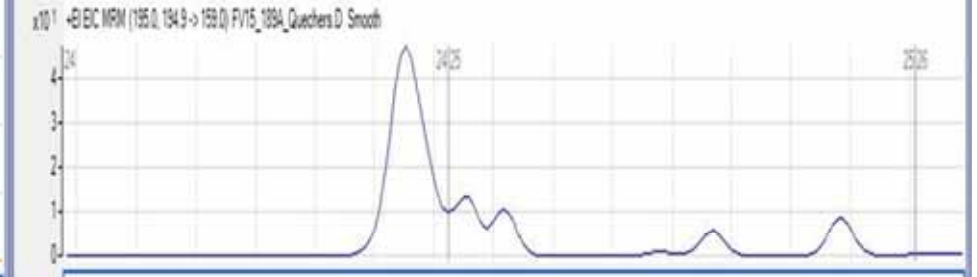
241>206



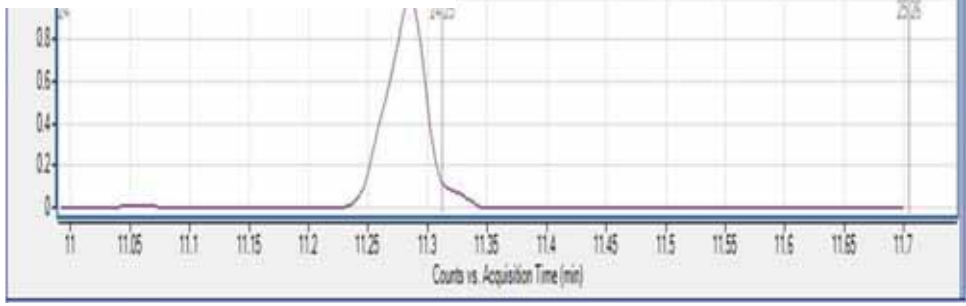


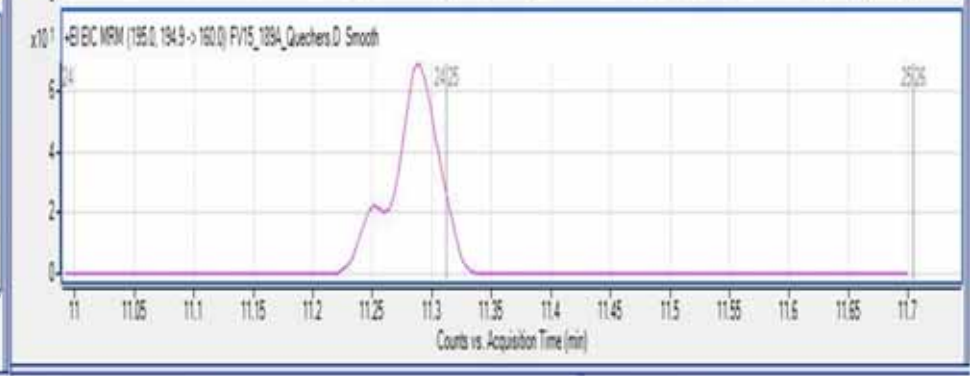
194.9>158





194.9>160





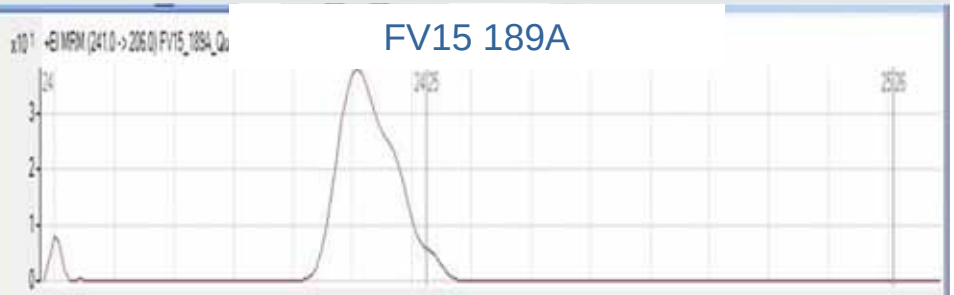
EURL-FV

EUPT-FV-15
European Proficiency Test FV-15

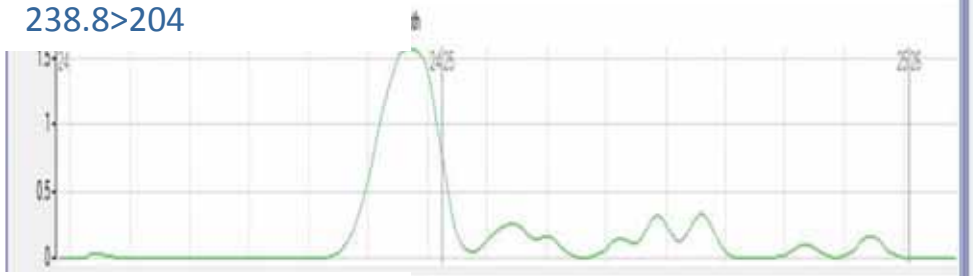
Endosulfan Beta (concentration < 10 µg/kg)

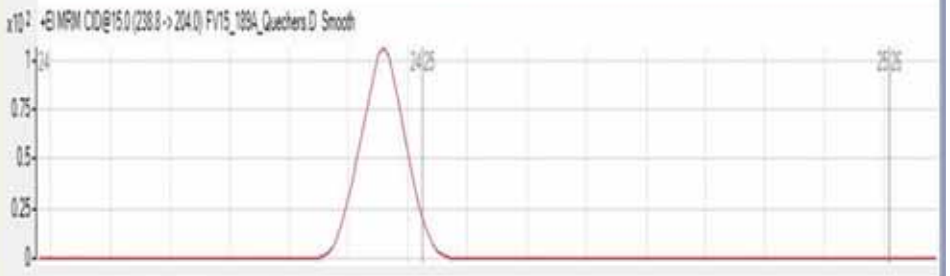
241>206 Std. 5 µg/kg Potato

FV15 189A

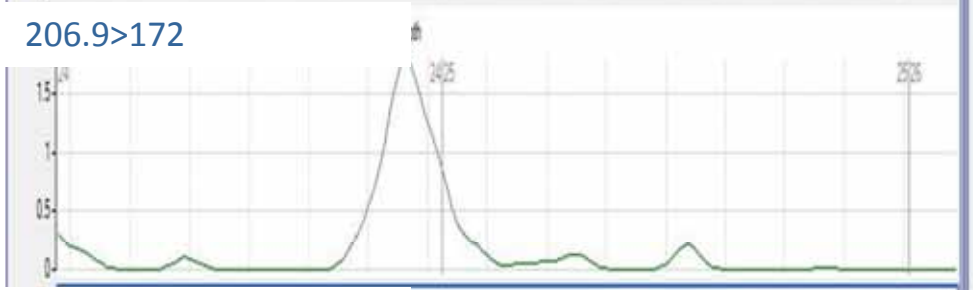


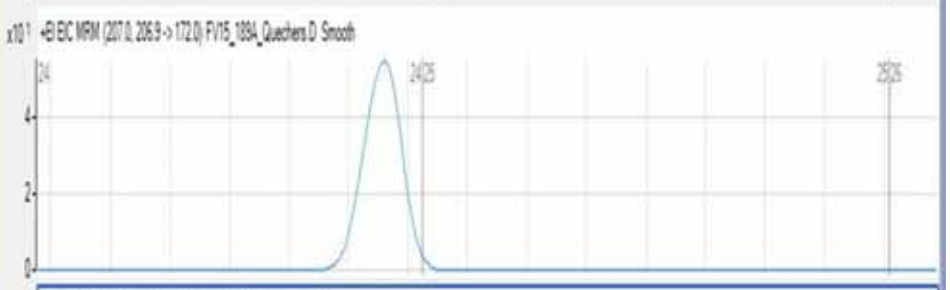
238.8>204



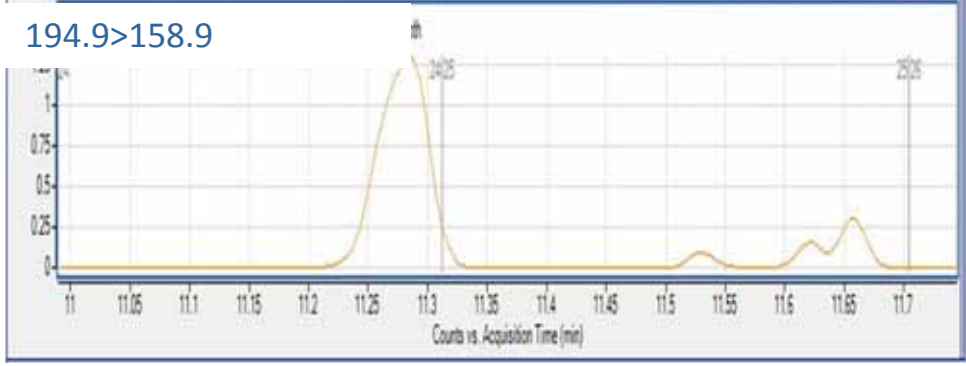


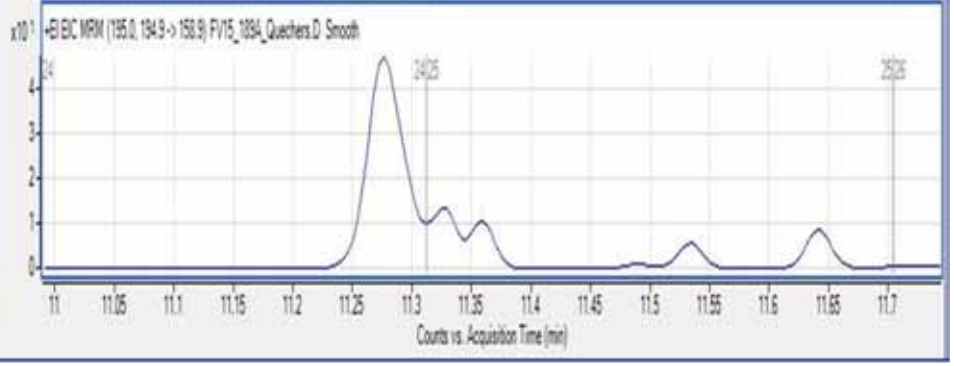
206.9>172





194.9>158.9





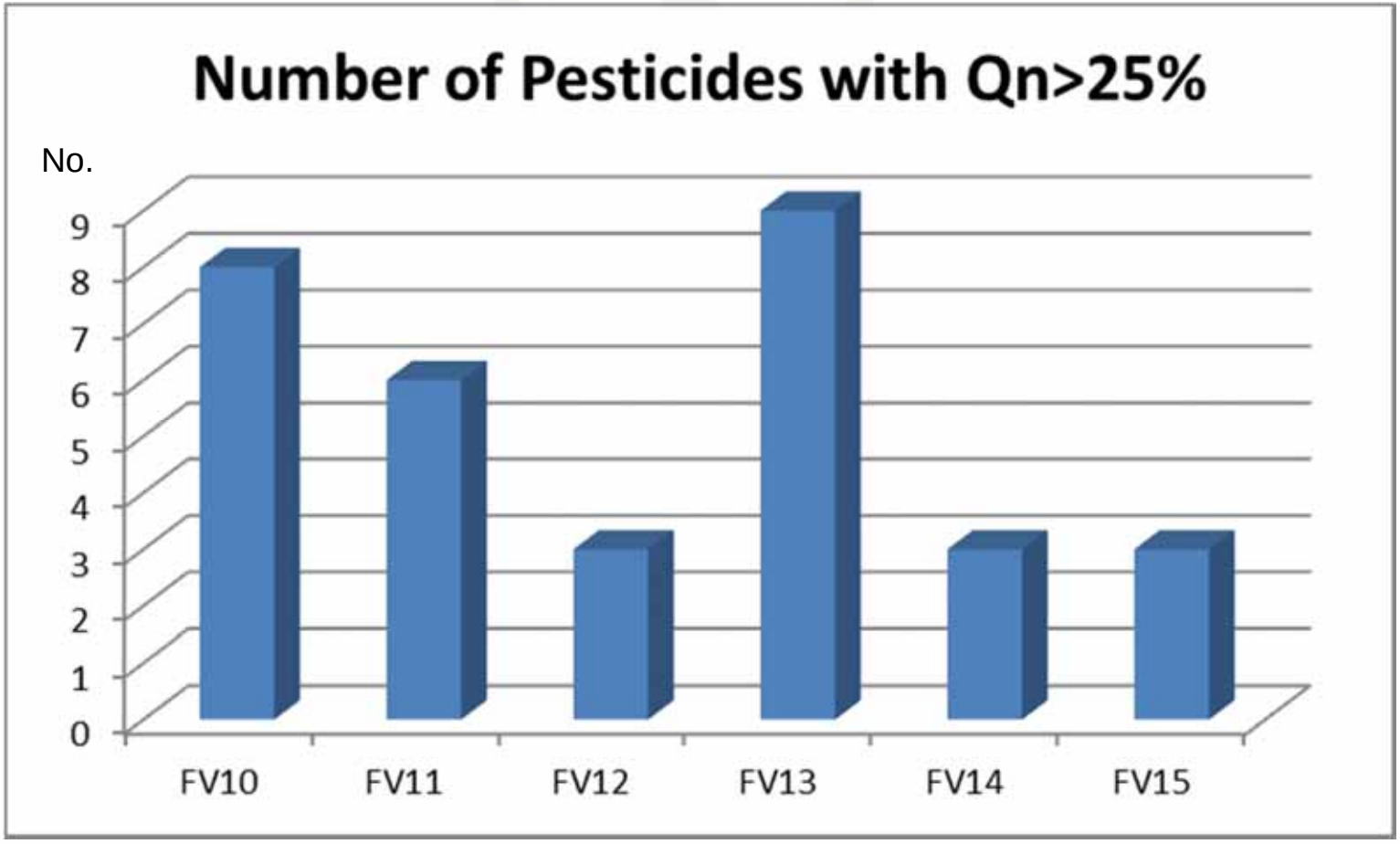
European Union Reference Laboratory for Pesticide Residues in Fruits & Vegetables

EUPT-FV-15

European Proficiency Test FV-15

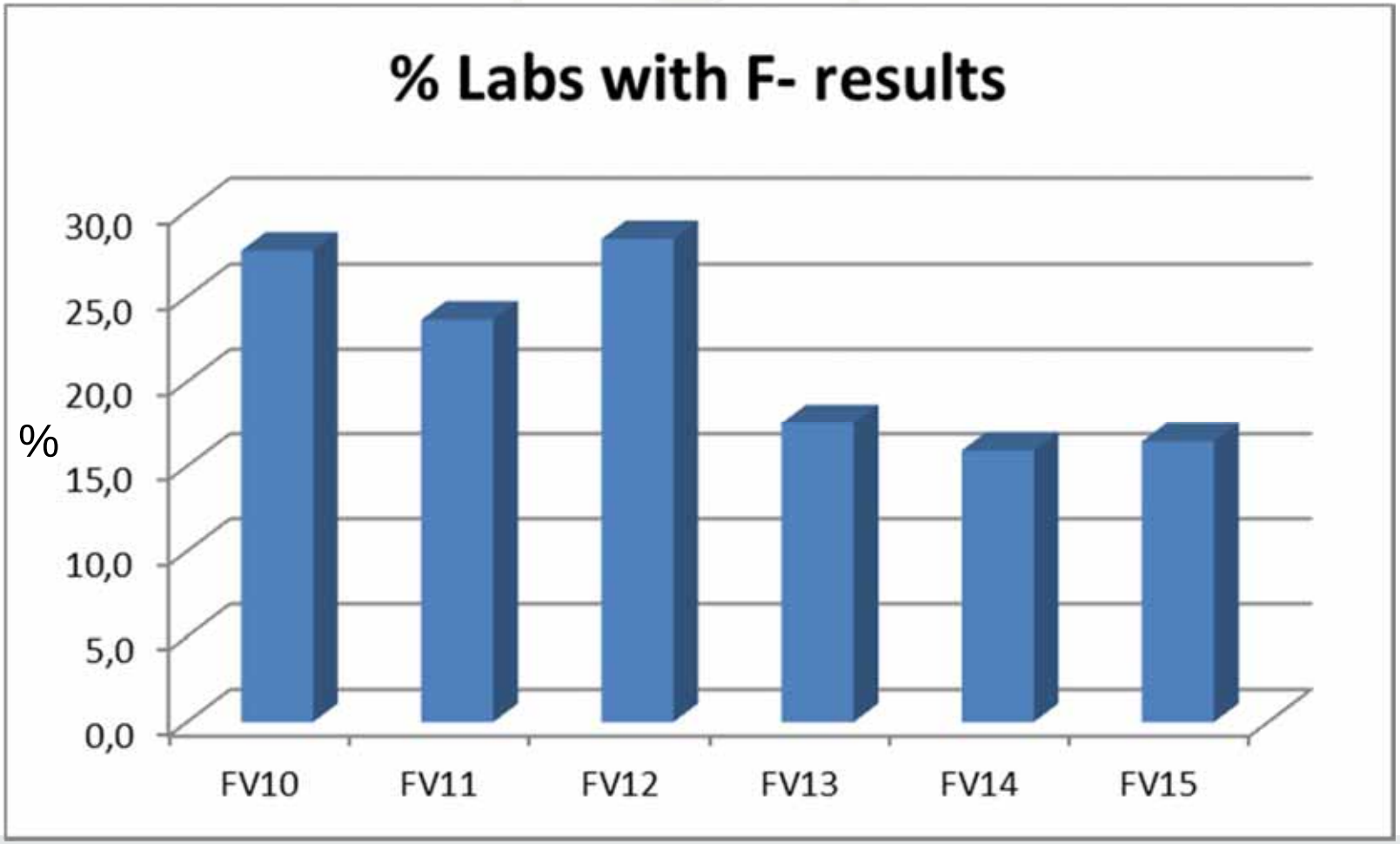
Evolution of the laboratories performance throughout the years

Dispersion of results



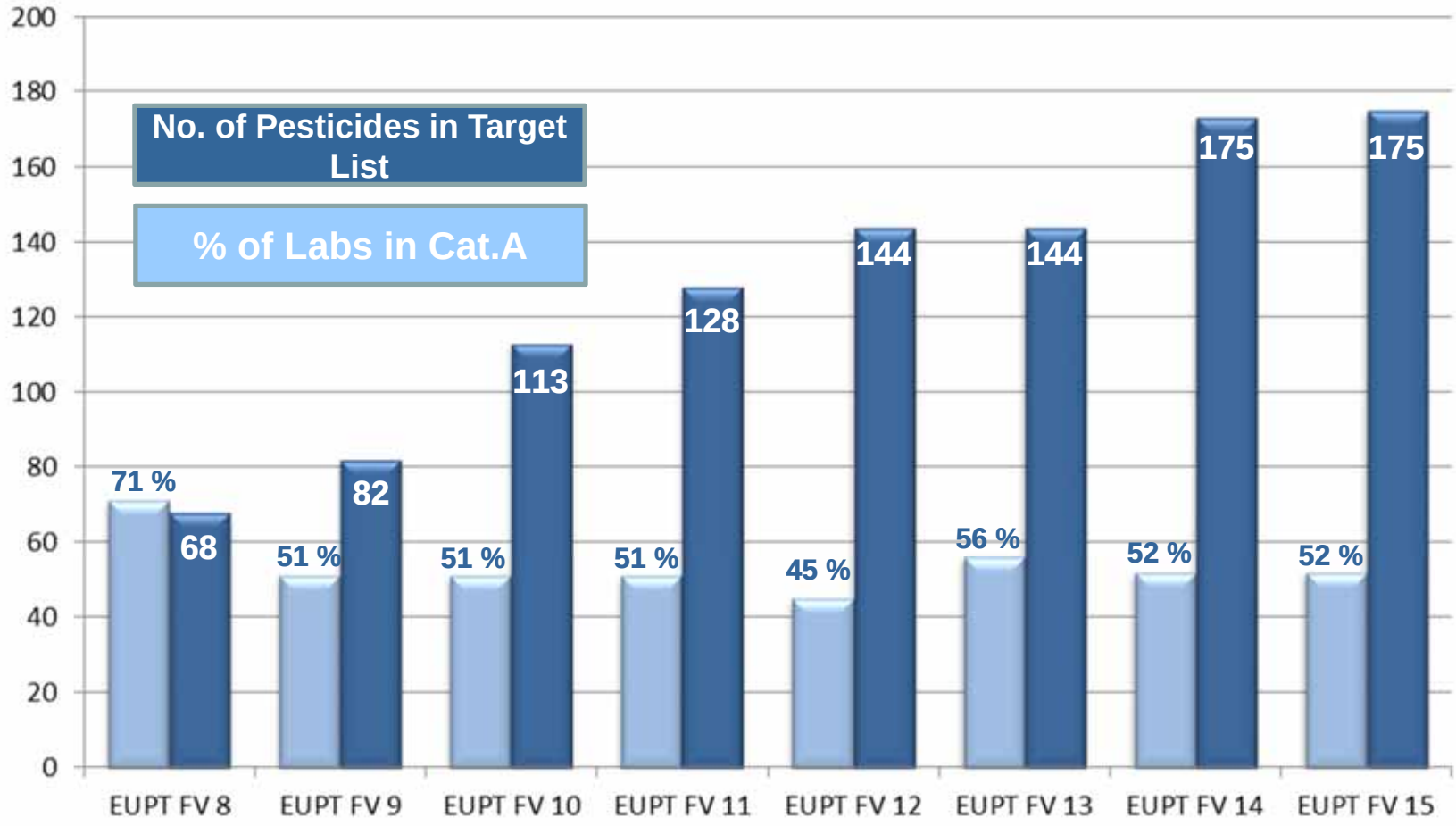
Evolution of the laboratories performance throughout the years

False Negatives



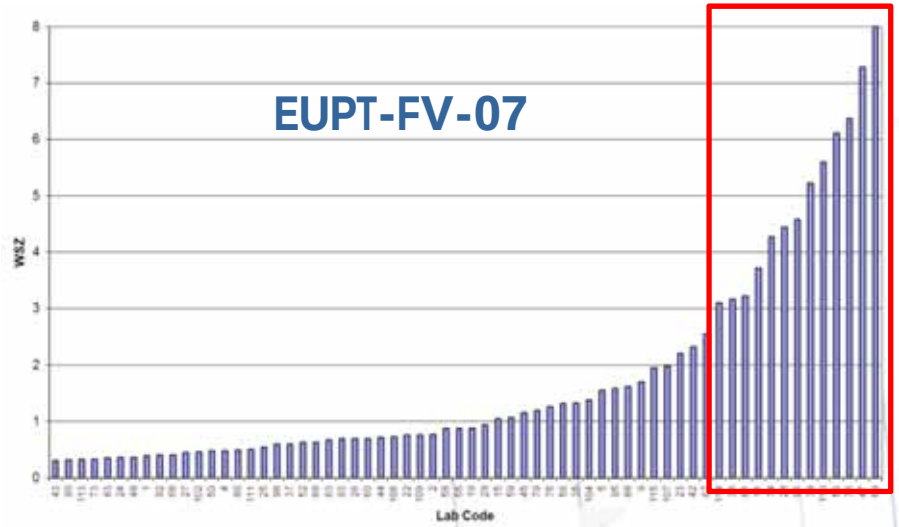
Evolution of the laboratories performance throughout the years

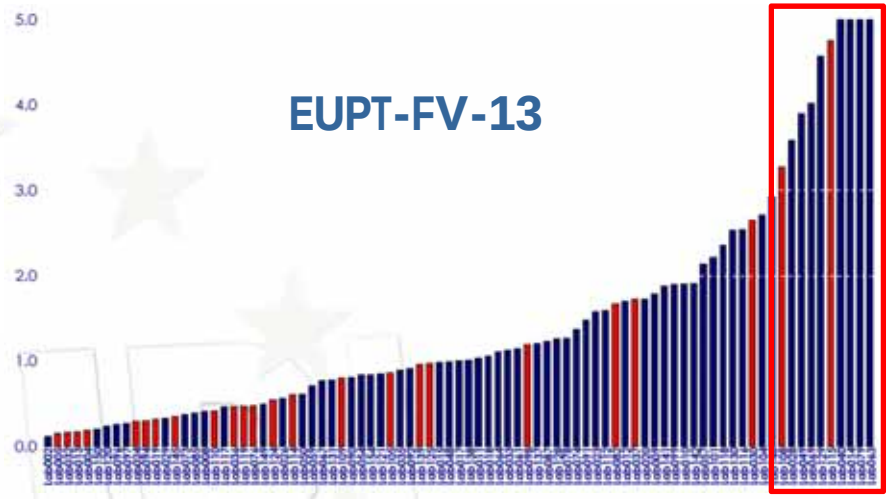
Labs in Category A

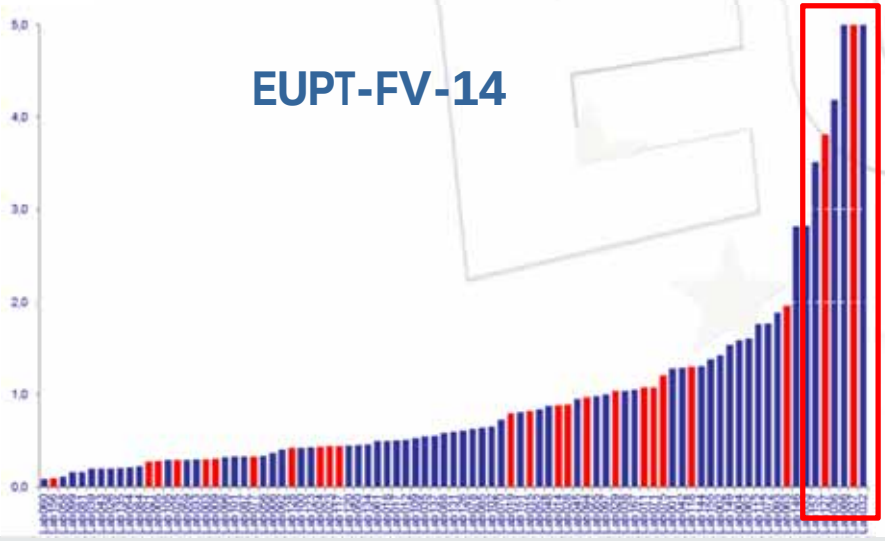


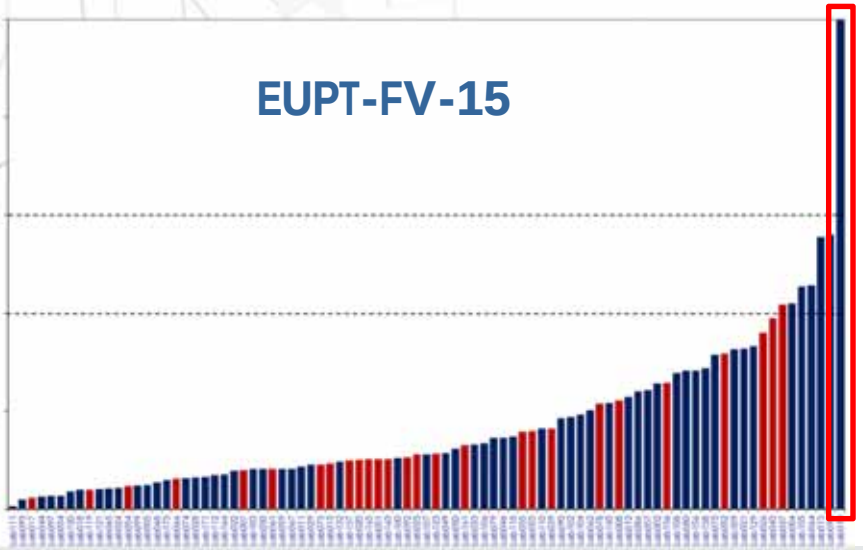
Evolution of the laboratories performance throughout the years

Labs in Category A



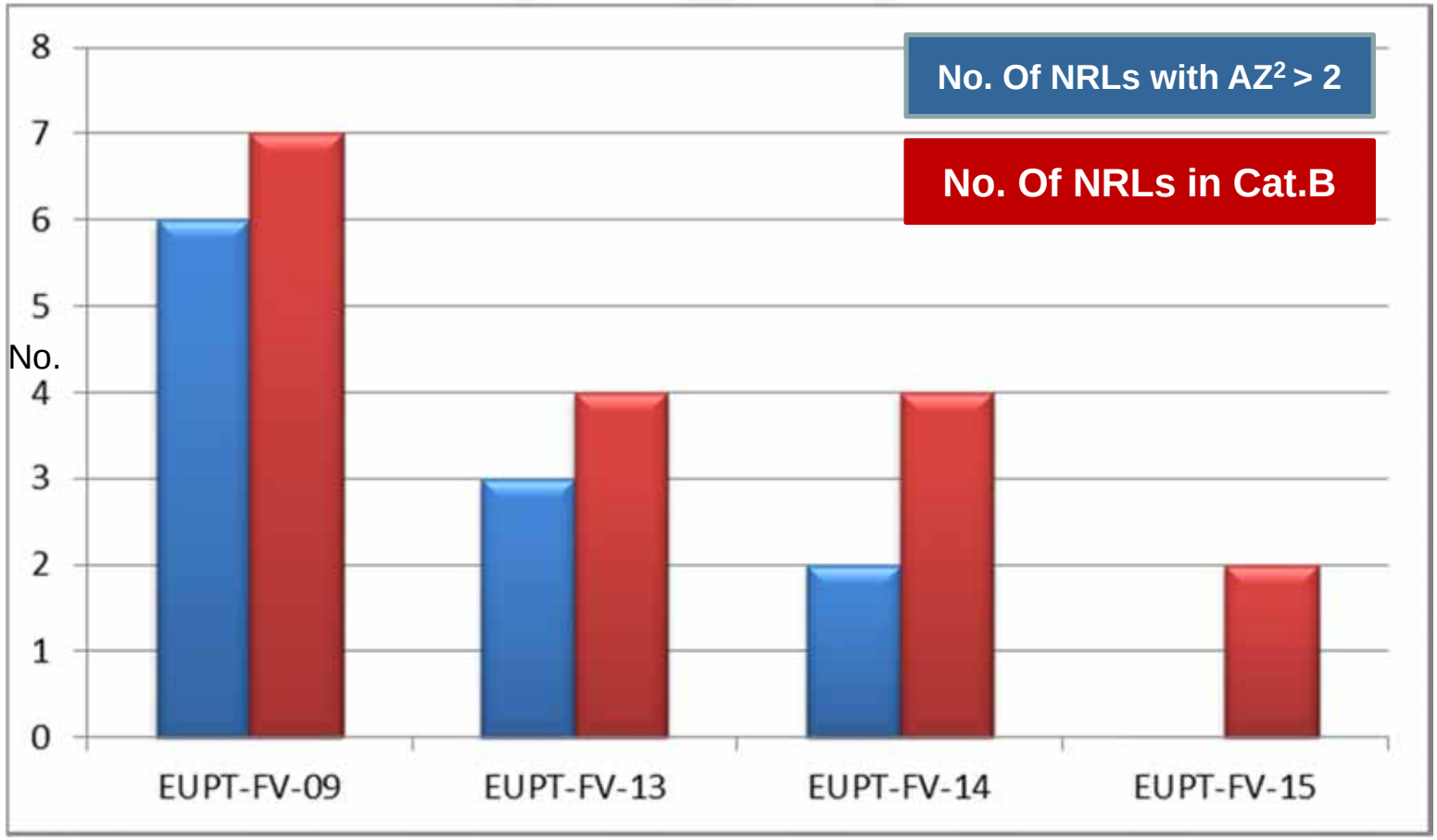






Evolution of the laboratories performance throughout the years

National Reference Laboratories



Evolution of the laboratories performance throughout the years

Common Pesticides

Spirodiclofen

New in EUPT-FV14 Target List

Present in EUPT-FV14 and EUPT-FV15 Test Item

	% of Reported Results	% of False Negative results
EUPT-FV-14	58	3
EUPT-FV-15	66	1

	% of z-scores		
	Acceptable	**Questionable**	**Unacceptable**
EUPT-FV-14	89	2.0	9.0
EUPT-FV-15	91	4.5	4.5

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Common Pesticides

Thiabendazole

	% of z-scores		
	Acceptable	**Questionable**	**Unacceptable**
EUPT-FV-13	83	8	8
EUPT-FV-14	97	1	2
EUPT-FV-15	95	3	1

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Common Pesticides

Iprodione

	% of z-scores		
	Acceptable	**Questionable**	**Unacceptable**
EUPT-FV-07	85	3	11
EUPT-FV-09	86	4	10
EUPT-FV-14	93	2	5

Conclusions

- Proficiency Tests are an efficient evaluation system, as they allow to follow the performance of the laboratories network.

- Throughout the years the results of the PTs have improved, although the laboratories should put their efforts into increasing the number of pesticides in their scope.

- The introduction of new pesticides in the target list provides an incentive for the laboratories to expand their scope.

Conclusions

- At least one laboratory from each Member State participated in EUPT-FV-15.
- Overall, the results were very good. Laboratories generally achieved accurate results for all the pesticides present in the test item.
- The concentration of the pesticides did not affect the results within the range of concentrations of this PT.
- No differences between the results obtained by different methods of analysis were observed.

Thank you for your Attention