

4th Joint Workshop of the EUROPEAN UNION REFERENCE LABORATORIES



Almeria
(SPAIN) 23rd-25th OCT
2013

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

EUPT-FV-15



European
Commission

EURL



CARMEN FERRER

EUROPEAN UNION REFERENCE LABORATORIES

EUPT-Panel

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Dr. Sonja Masselter

Dr. Tuija Pihlström

Dr. Mette Erecius Poulsen

Dr. Darinka Stajnbaher

Participation



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

EU/EFTA Labs = 162

Other countries Labs = 13

Total No. of Countries = 40

EU/EFTA countries = 30

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**

175 pesticides

Clofentezine	
3-hydroxy-carbofuran	Clothianidin
Acephate	Cyfluthrin
Acetamiprid	Cypermethrin
Acrinathrin	Cyproconazole
Aldicarb	Cyprodinil
Aldicarb Sulfone	Deltamethrin
Aldicarb Sulfoxide	Demeton-S-methylsulfone
Amitraz	Desmethyl-pirimicarb
Azinphos-methyl	Diazinon
Azoxystrobin	Dichlofluanid
Benfuracarb	Dichlorvos
Bifenthrin	Dicloran
Bitertanol	Dicofol
Boscalid	Difenoconazole
Bromopropylate	Diflubenzuron
Bromuconazole	Dimethoate
Bupirimate	Dimethomorph
Buprofezin	DMST
Cadusafos*	Diphenylamine
Captan	DMF
Carbaryl	DMPF
Carbendazim	Endosulfan alpha
Carbofuran	Endosulfan beta
Carbosulfan	Endosulfan sulfate
Chlorfenapyr	EPN
Chlorfenvinphos	Epoxiconazole
Chlorobenzilate*	Ethion
Chlorothalonil	Ethoprophos
Chlorpropham	Etofenprox
Chlorpyrifos	Fenamiphos
Chlorpyrifos-methyl	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
- Flupicolide*
- Fluquinconazole
- Flusilazole
- Flutolanil*
- Flutriatol
- 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
Quinoxifen
Thiophanate-methyl
Tolclofos-methyl
Tolyfluanid
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 analytical 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 analyze [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:

Octavio Malato
omalato@ual.es

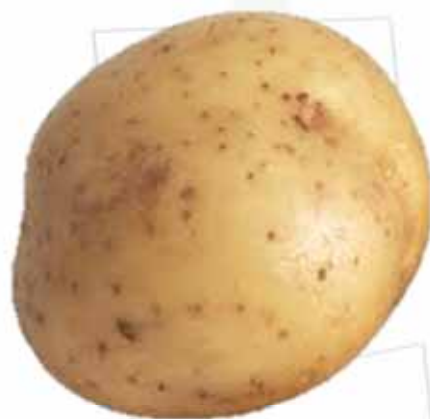
Carmen Ferrer
cferrer@ual.es

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EUPT-FV-15

European Proficiency Test FV-15



Potato





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





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4th Joint Workshop of the European Union Reference Laboratories for Residues of Pesticides

Homogeneity

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



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

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

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

January						
Su	Mo	Tu	We	Th	Fr	Sa
		1	2	3	4	5
6	7	8	9	10	11	12
13	14	15	16	17	18	19
20	21	22	23	24	25	26
27	28	29	30	31		

February						
Su	Mo	Tu	We	Th	Fr	Sa
					1	2
3	4	5	6	7	8	9
10	11	12	13	14	15	16
17	18	19	20	21	22	23
24	25	26	27	28		

Stability

Pesticide	Concentration (mg/kg)							%
	Day 1 (1 st analysis)	Day 1 (2 nd analysis)	Mean 1	Day 2 (1 st analysis)	Day 2 (2 nd analysis)	Mean 2	$\frac{(M2-M1)}{M1}$	
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
Chlorpyrifos	1.244	1.405	1.400	1.400	1.300	1.400	0.010	1
Cyfluthrin	0.051	0.051	0.051	0.051	0.051	0.051	0.000	-1
Diazinon	0.051	0.051	0.051	0.051	0.051	0.051	0.000	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

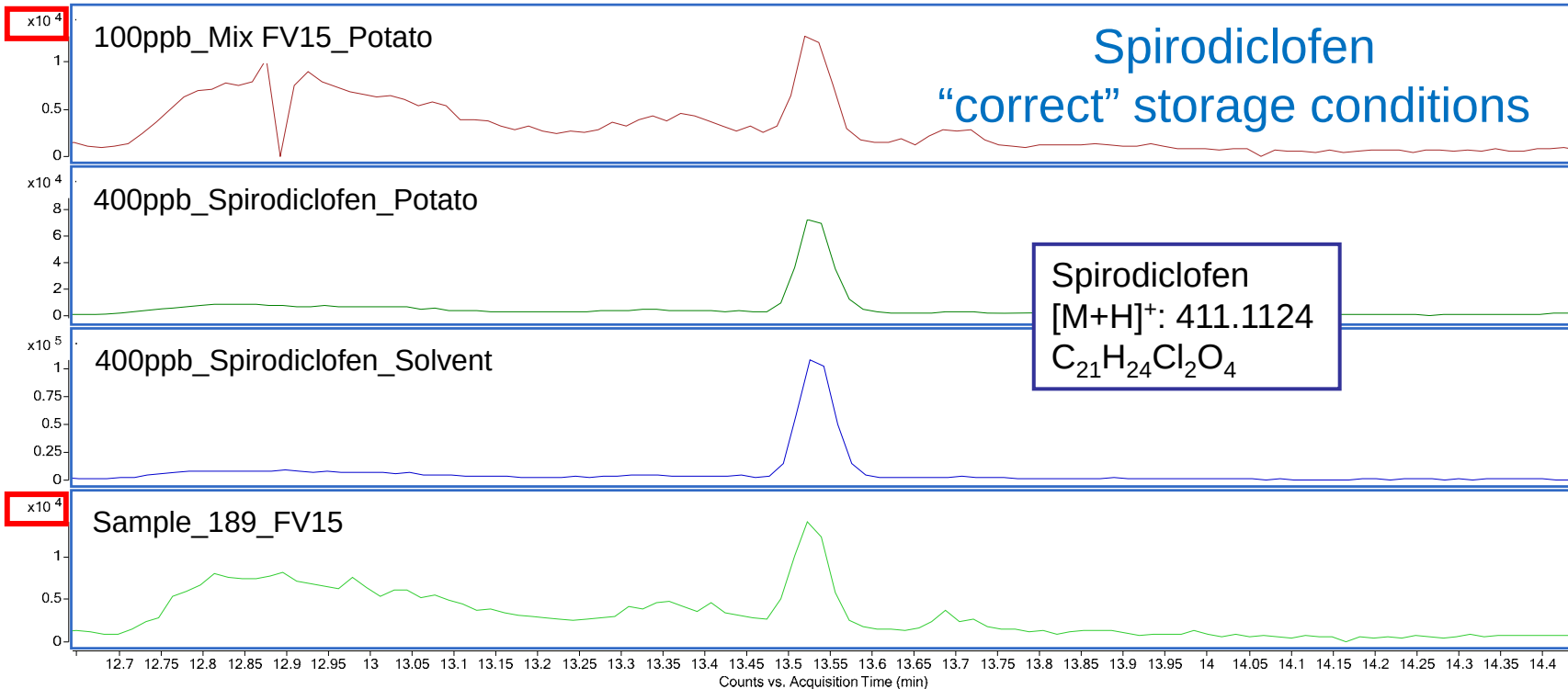
January						
Su	Mo	Tu	We	Th	Fr	Sa
		1	2	3	4	5
6	7	8	9	10	11	12
13	14	15	16	17	18	19
20	21	22	23	24	25	26
27	28	29	30	31		

February						
Su	Mo	Tu	We	Th	Fr	Sa
					1	2
3	4	5	6	7	8	9
10	11	12	13	14	15	16
17	18	19	20	21	22	23
24	25	26	27	28		

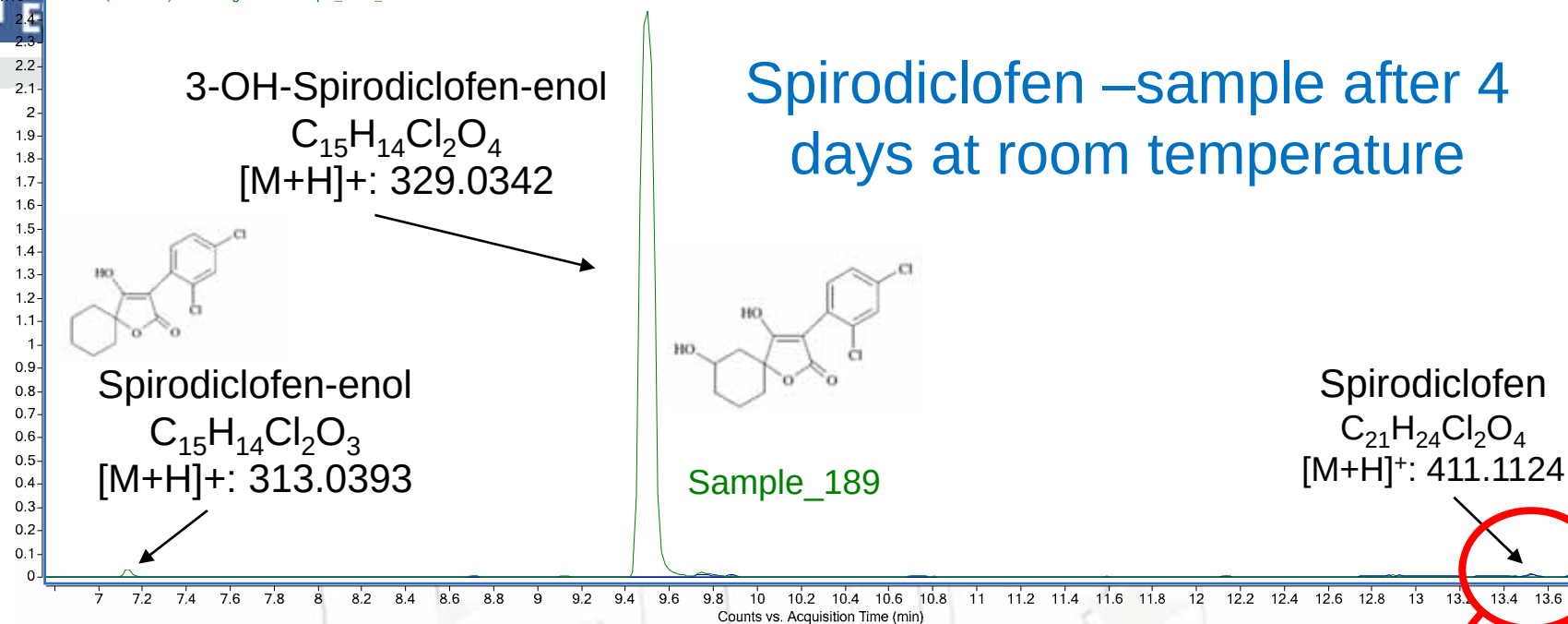
Stability

Pesticide	Concentration (mg/kg)							%
	Day 1 (1 st analysis)	Day 1 (2 nd analysis)	Mean 1	48h (1 st analysis)	48h (2 nd analysis)	Mean 2	$\frac{(M2-M1)}{M1}$	
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

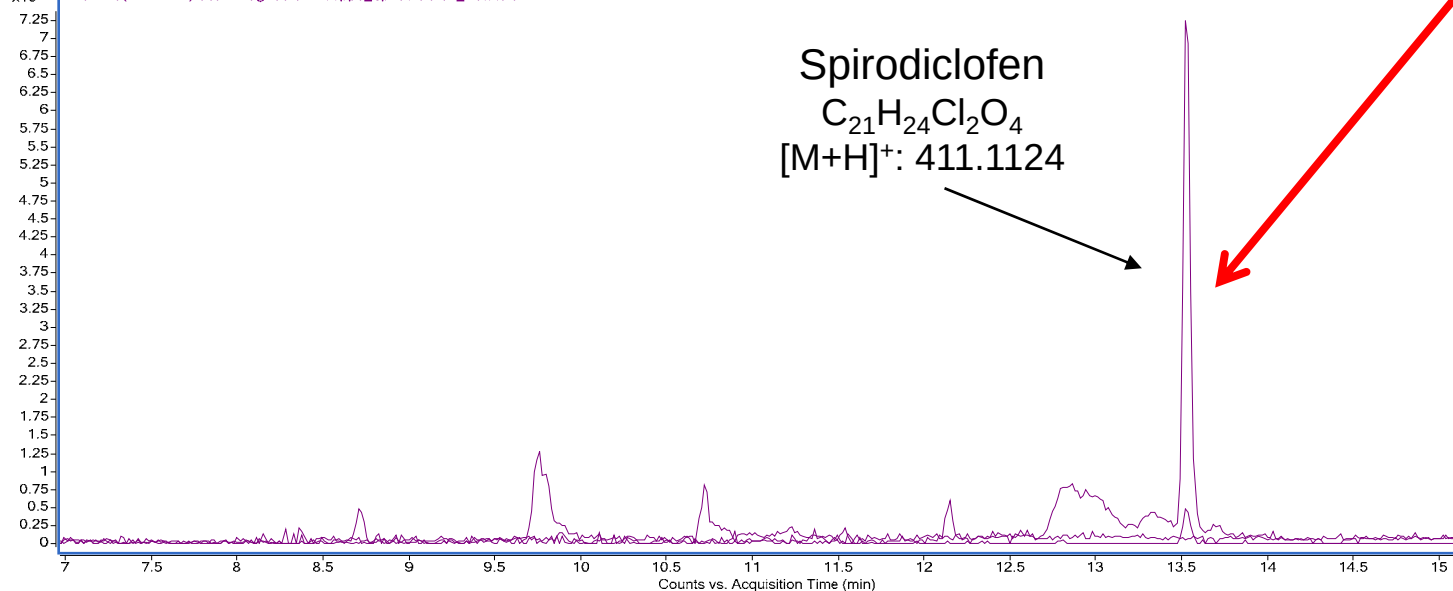
All the pesticides passed the stability test

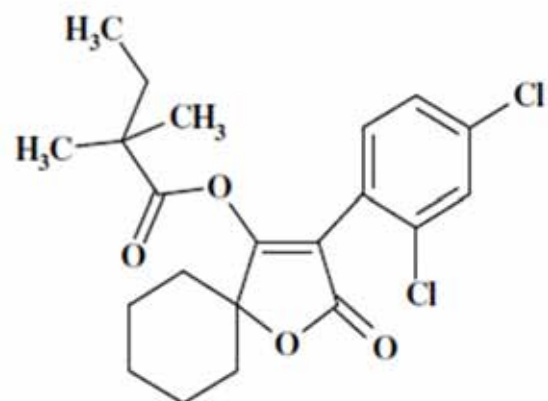


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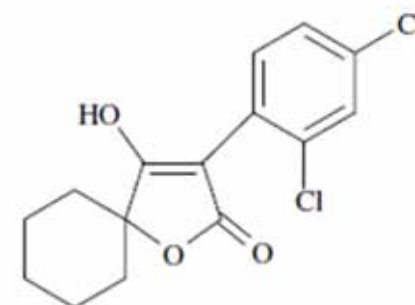


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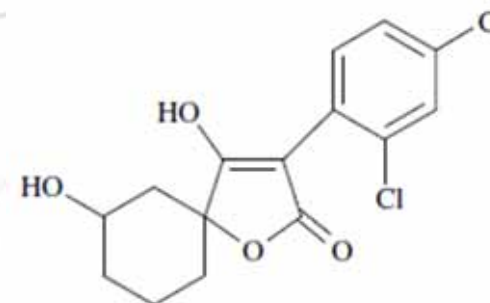




Spirodiclofen

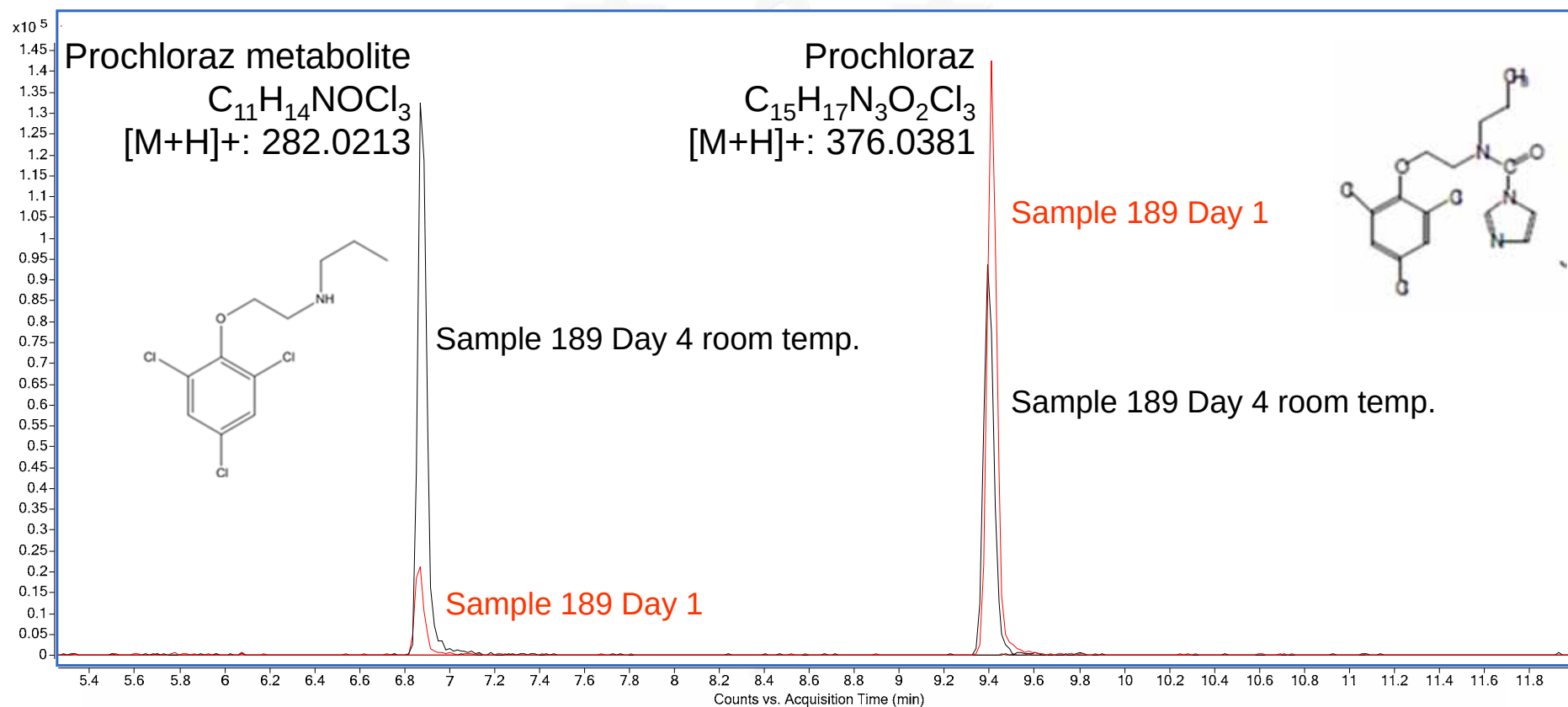


Spirodiclofen-enol



3-hydroxy-spirodiclofen-enol

PROCHLORAZ- Potato sample at room temperature during 4 days





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Almería 23rd-25th October 2013

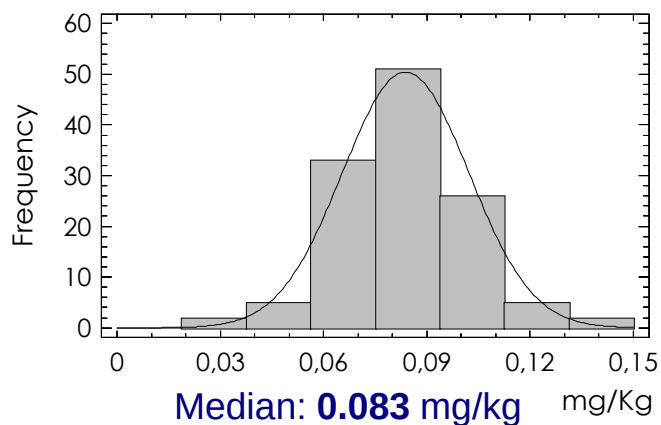
EUPT-FV-15
European Proficiency Test FV-15

RESULTS

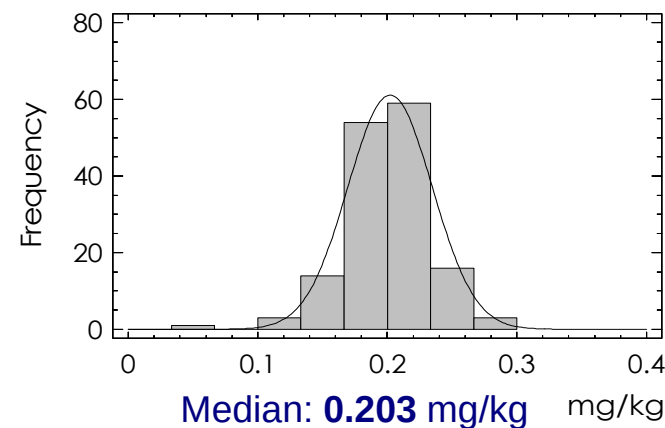
EURL

Distribution of data-Histograms

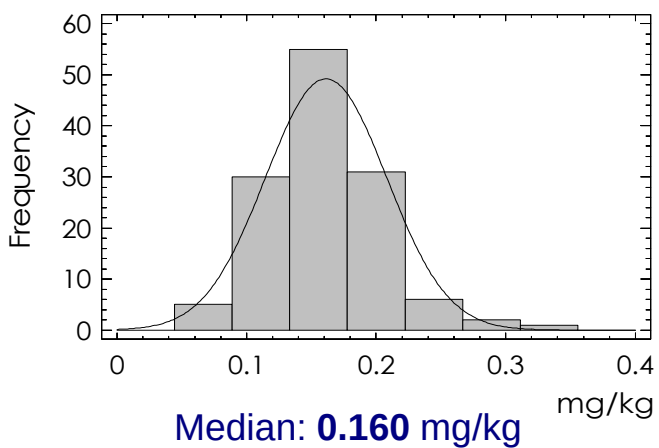
Acephate



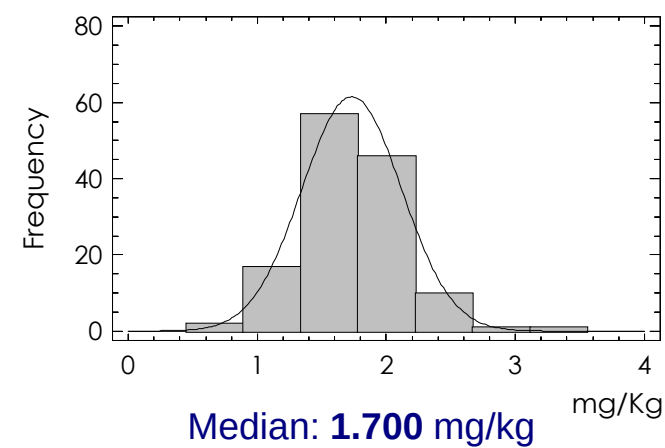
Azoxystrobin



Chlorothalonil

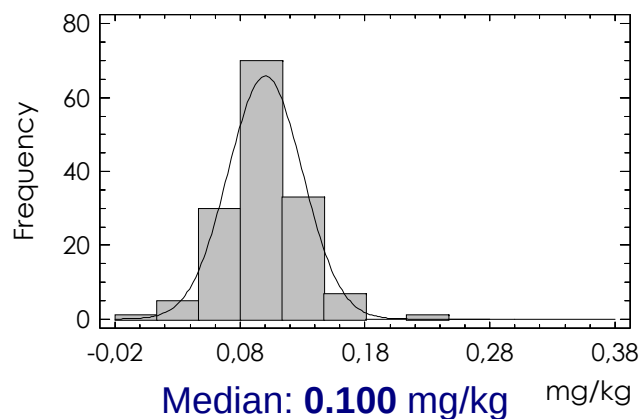


Chlorpropham

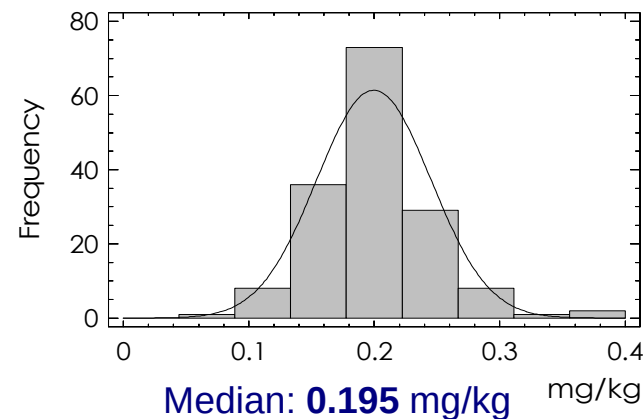


Distribution of data-Histograms

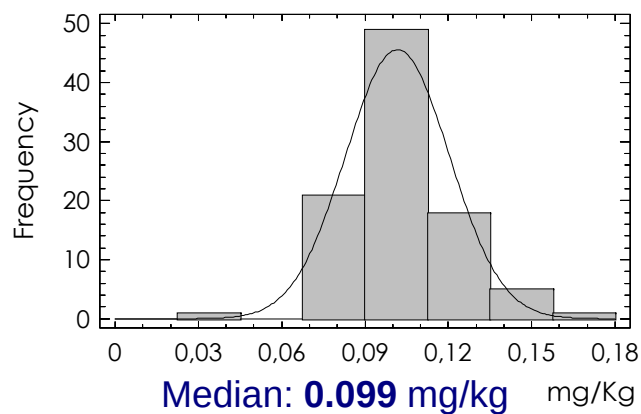
Cypermethrin



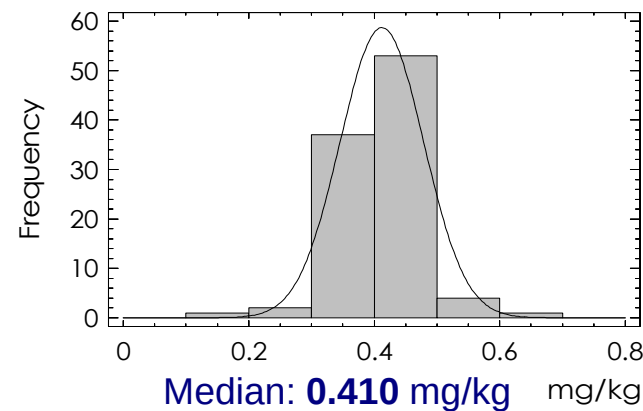
Diazinon



Fluopicolide

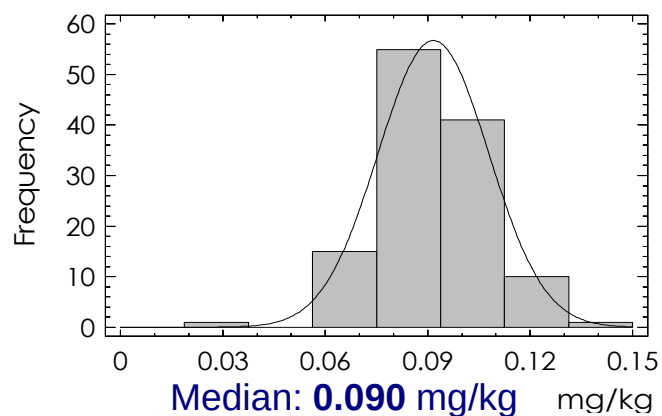


Flutolanil

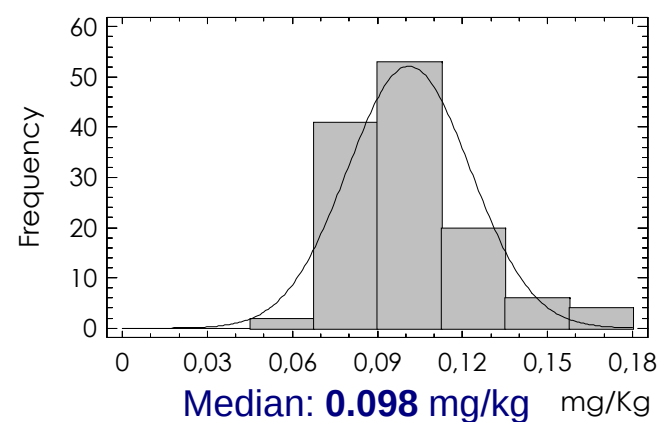


Distribution of data-Histograms

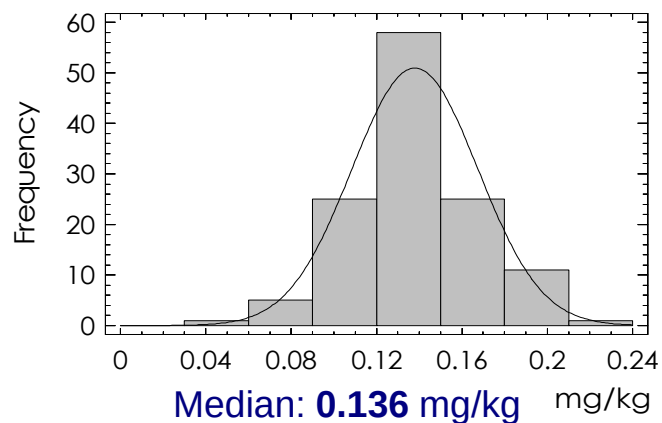
Iprovalicarb



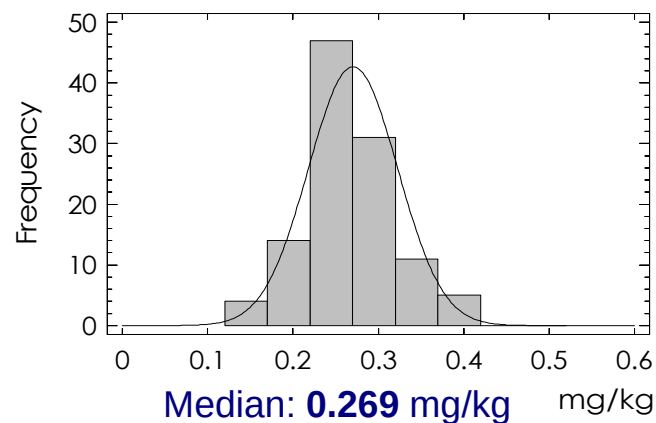
Linuron



Methiocarb

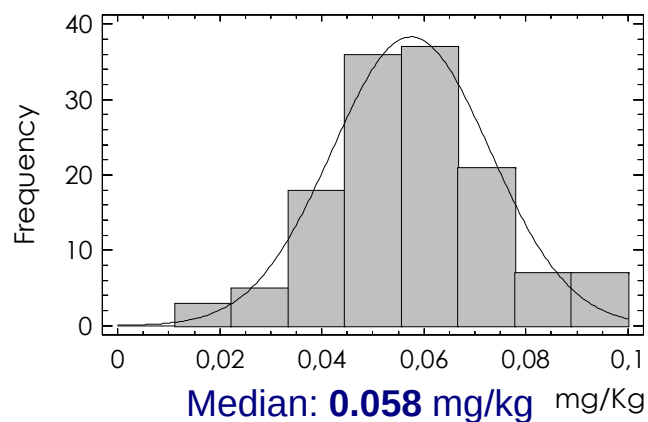


Pencycuron

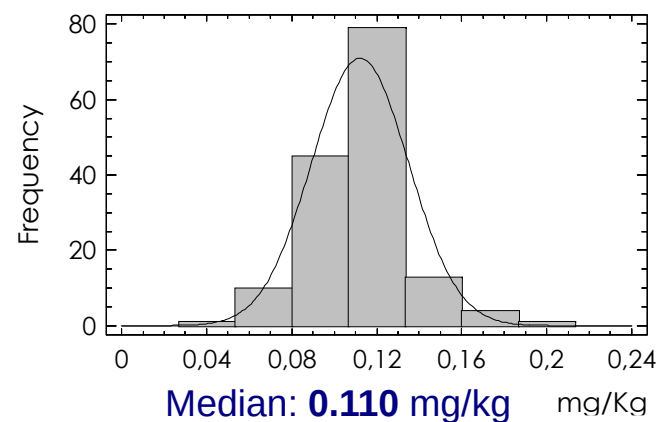


Distribution of data-Histograms

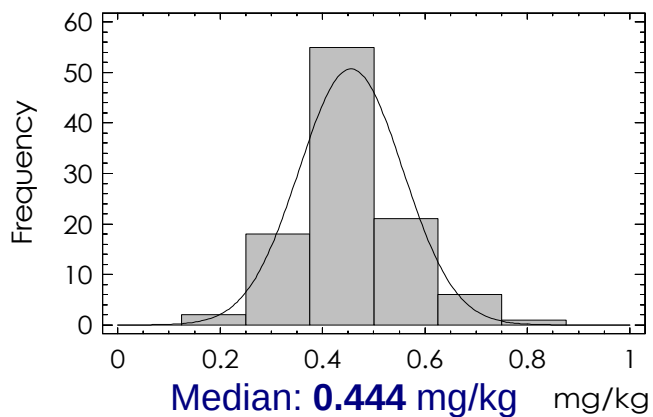
Prochloraz



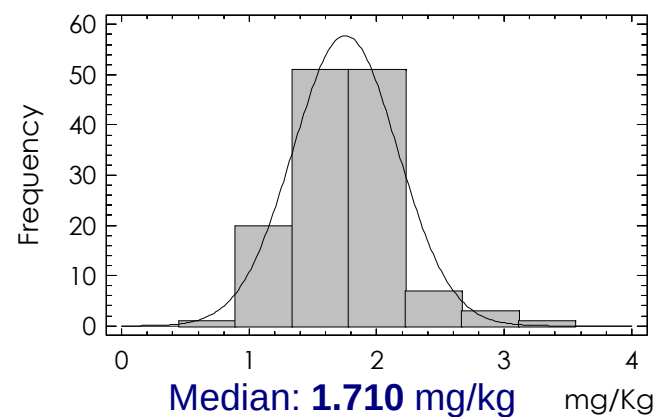
Procymidone



Spirodiclofen

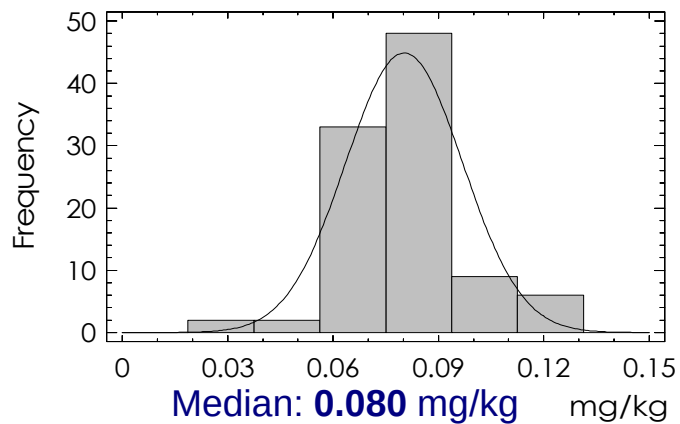


Thiabendazole

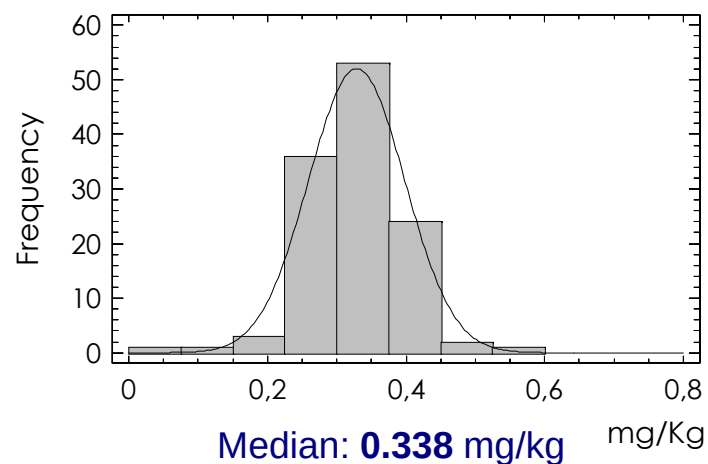


Distribution of data-Histograms

Fosthiazate



Thiacloprid



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

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

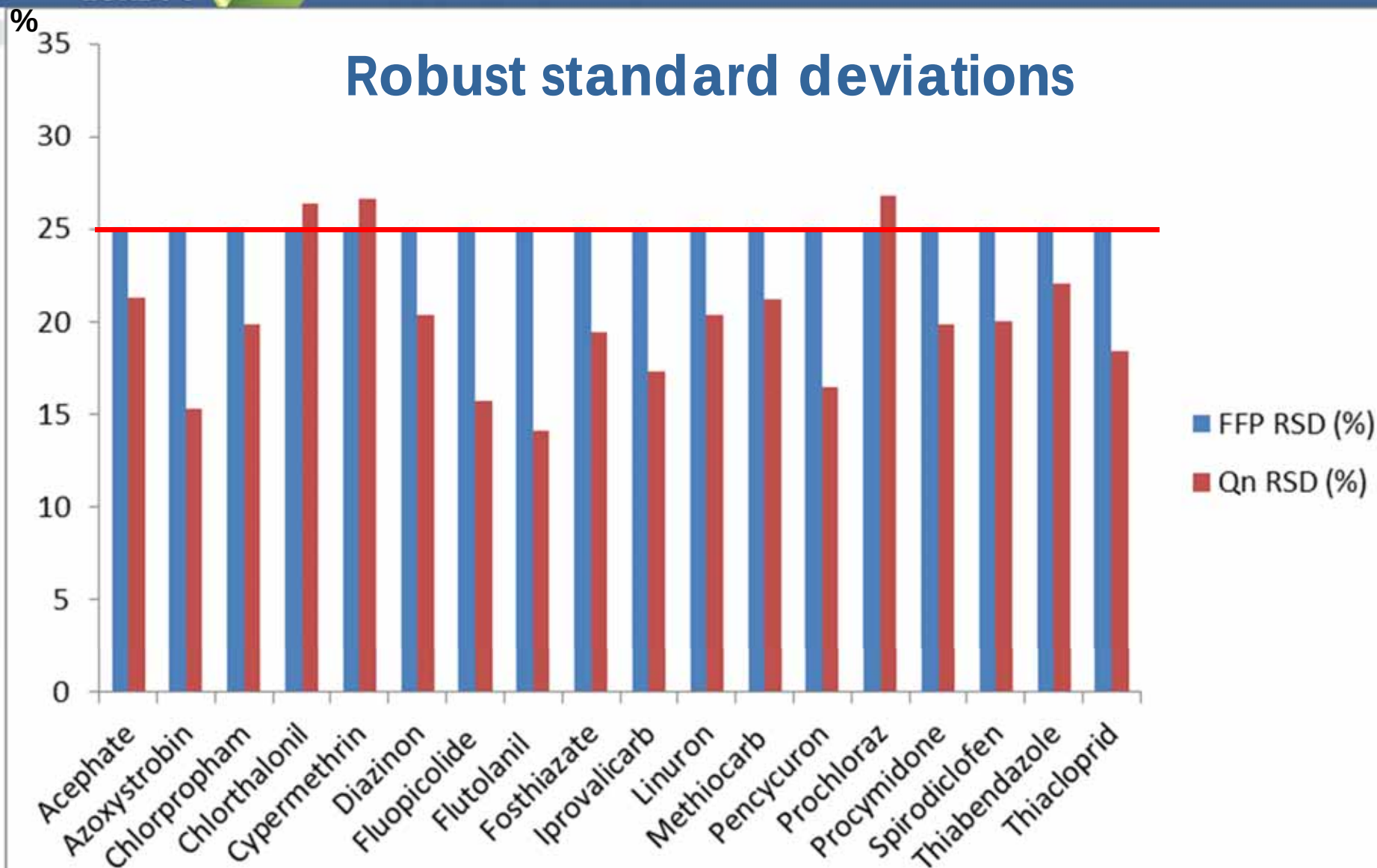
0.058-0.100 mg/kg

0.100-0.500 mg/kg

0.500-2.000 mg/kg

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

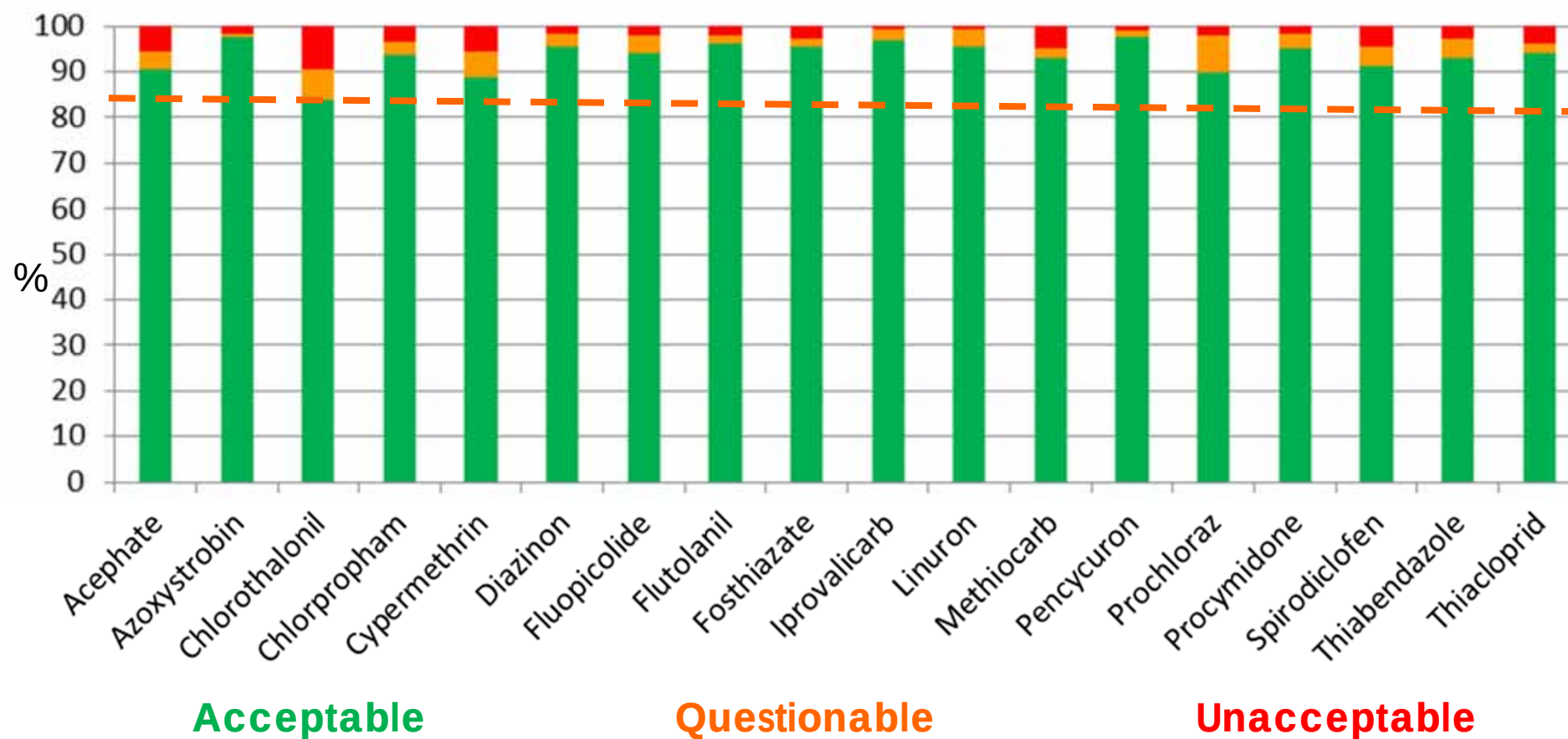


Pesticides	No. of Reported Results	No. of False Negative Results	No. of Not Analysed Results	Percentage of Reported Results (out of 160)
Acephate	124	8	28	78
Azoxystrobin	151	1	8	94
Chlorothalonil	134	5	21	84
Chlorpropham	134	3	23	84
Cypermethrin	146	6	8	91
Diazinon	159	0	1	99
Fluopicolide	95	0	65	59
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



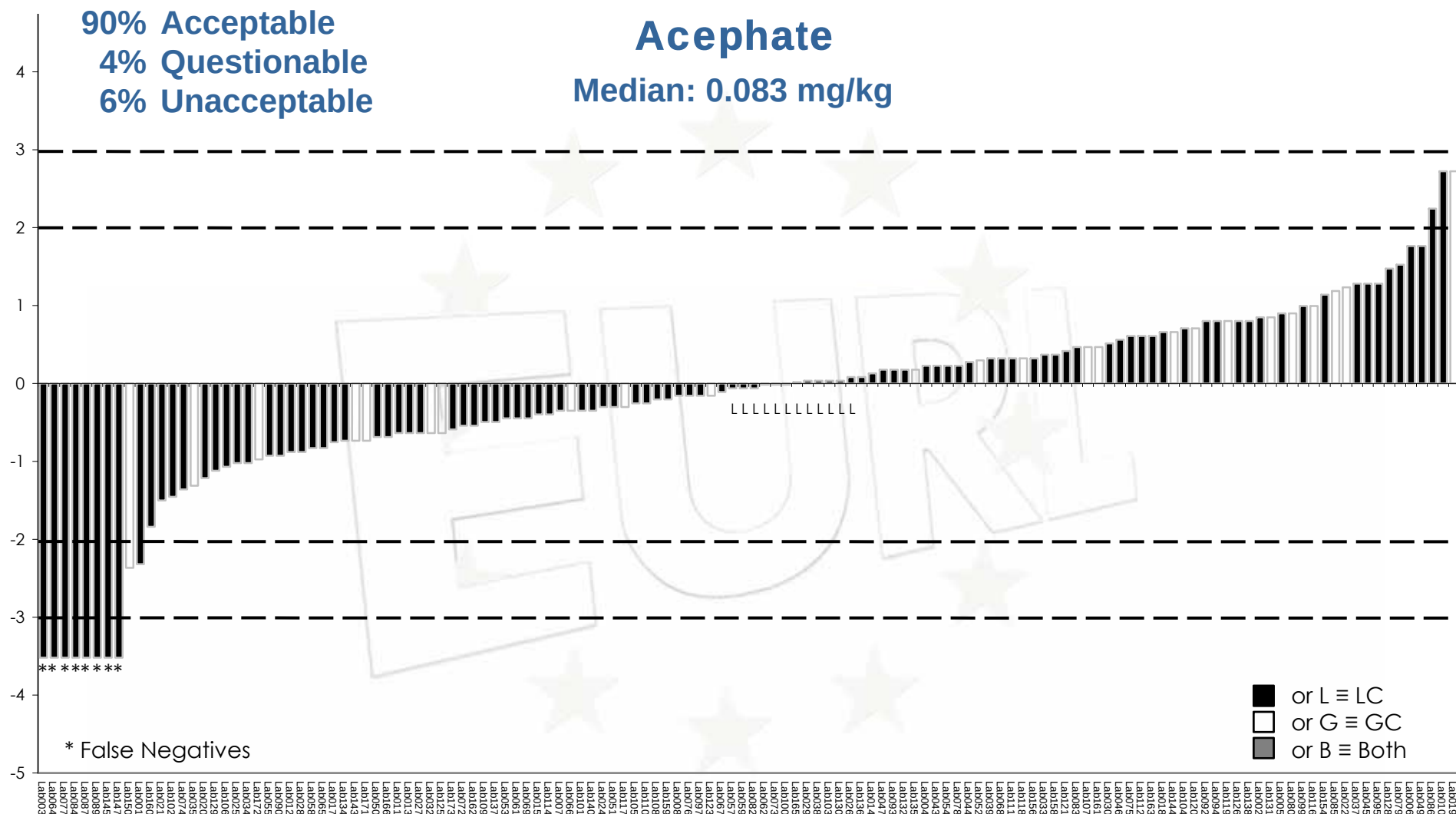
z-Scores

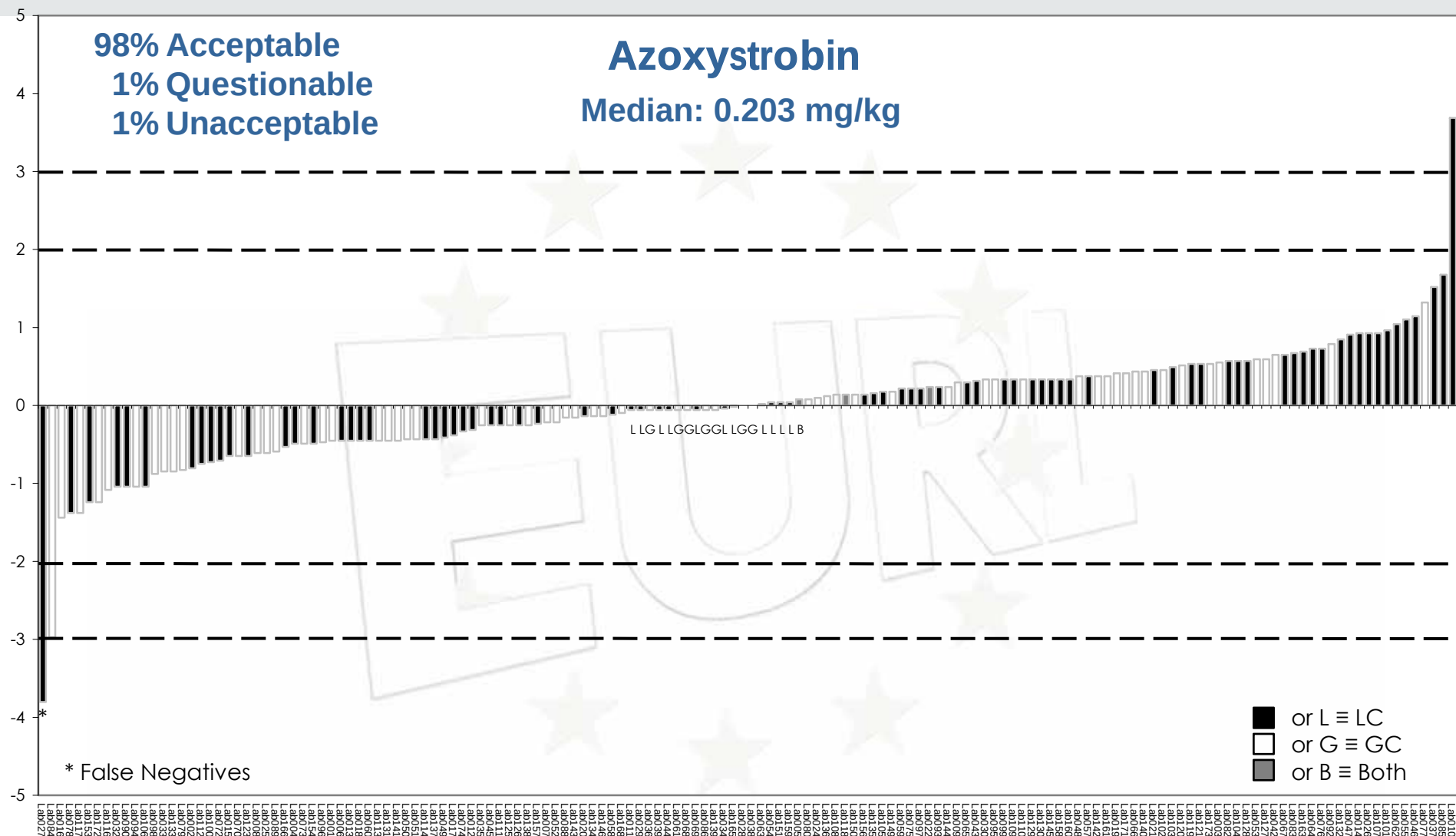
z-Scores classification

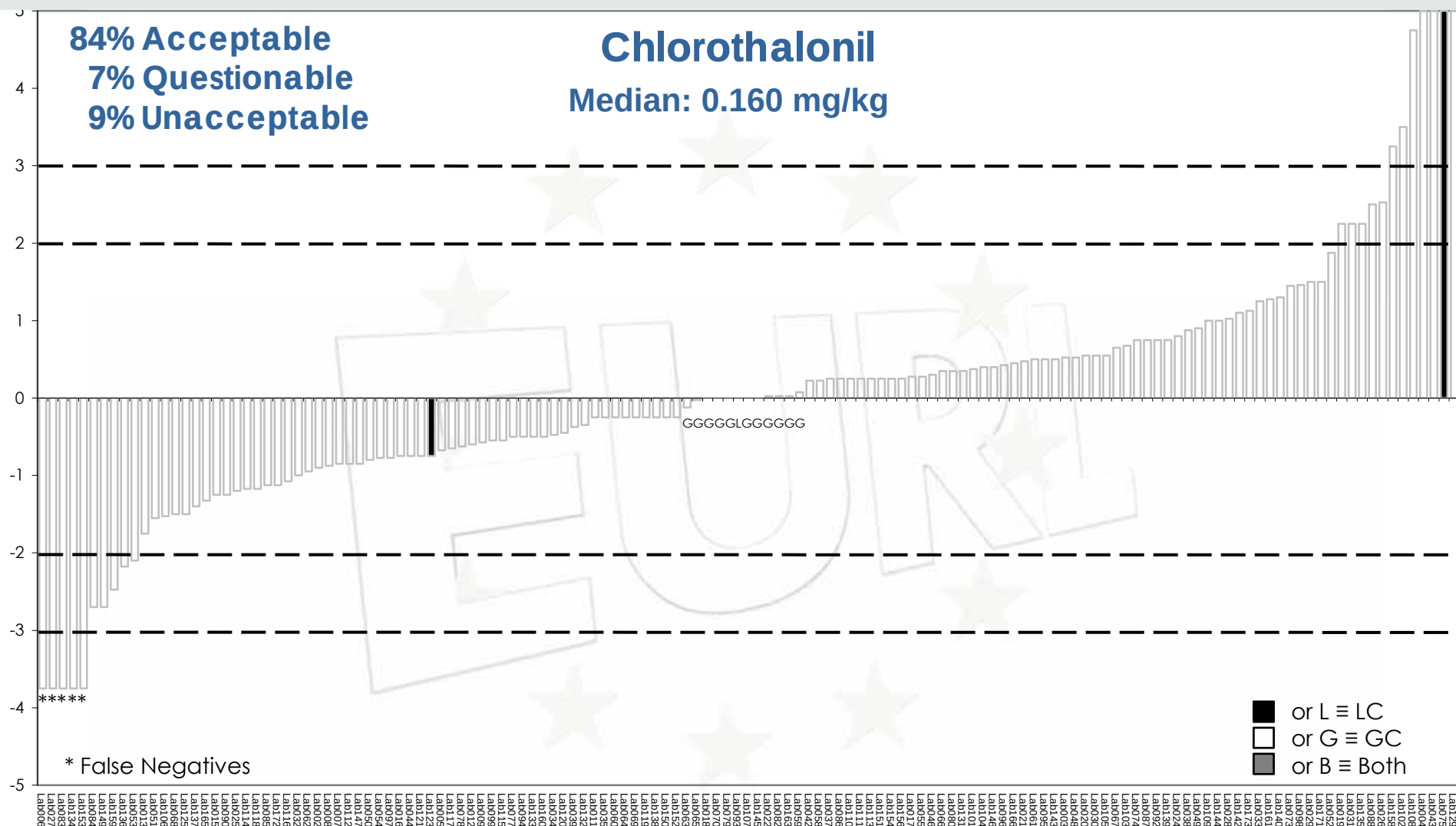


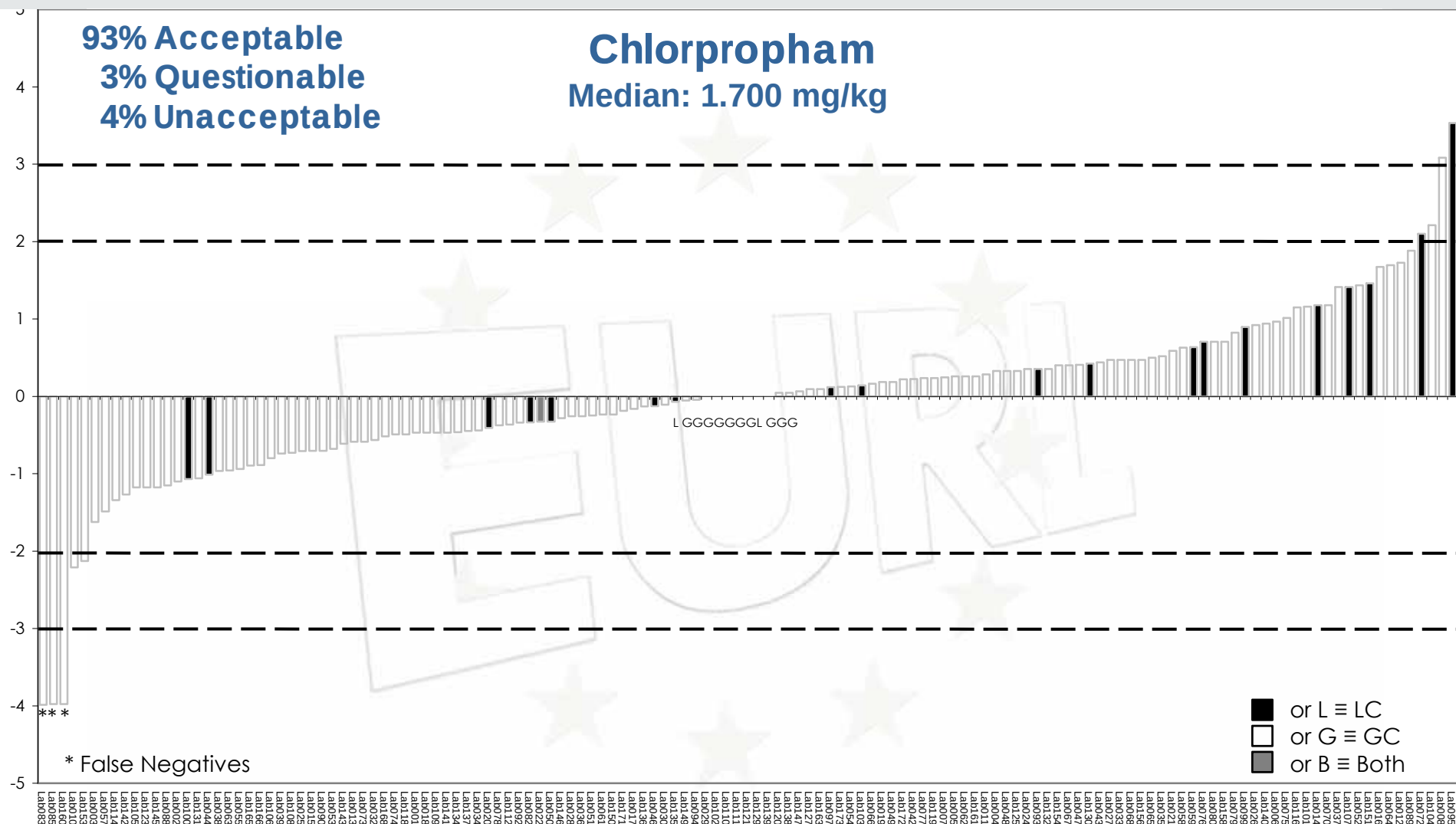
Pesticides	Median (mg/kg)	Acceptable (%)	Questionable (%)	Unacceptable (%)
Acephate	0.083	90.1	3.8	6.1
Azoxystrobin	0.203	98.0	0.7	1.3
Chlorothalonil	0.160	83.5	7.2	9.3
Chlorpropham	1.700	93.4	3.0	3.6
Cypermethrin	0.100	89.4	6.0	4.6
Diazinon	0.195	95.0	3.1	1.9
Fluopicolide	0.099	95.7	4.3	0.0
Flutolanil	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

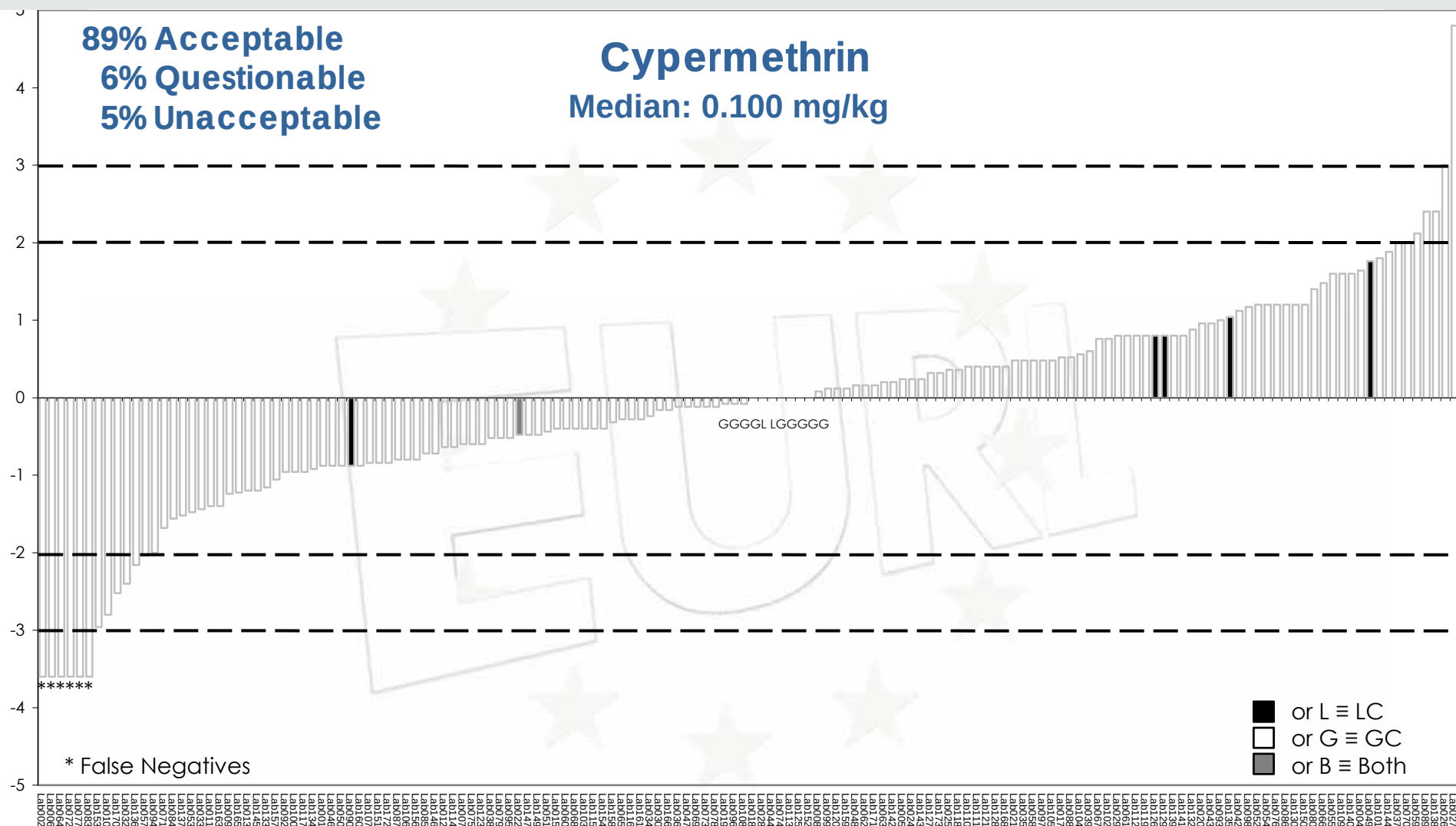
Pesticides	Median (mg/kg)	Acceptable (%)	Questionable (%)	Unacceptable (%)
Acephate	0.083	90.1	3.8	6.1
Azoxystrobin	0.203	98.0	0.7	1.3
Chlorothalonil	0.160	83.5	7.2	9.3
Chlorpropham	1.700	93.4	3.0	3.6
Cypermethrin	0.100	89.4	6.0	4.6
Diazinon	0.195	95.0	3.1	1.9
Fluopicolide	0.099	95.7	4.3	0.0
Flutolanil	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

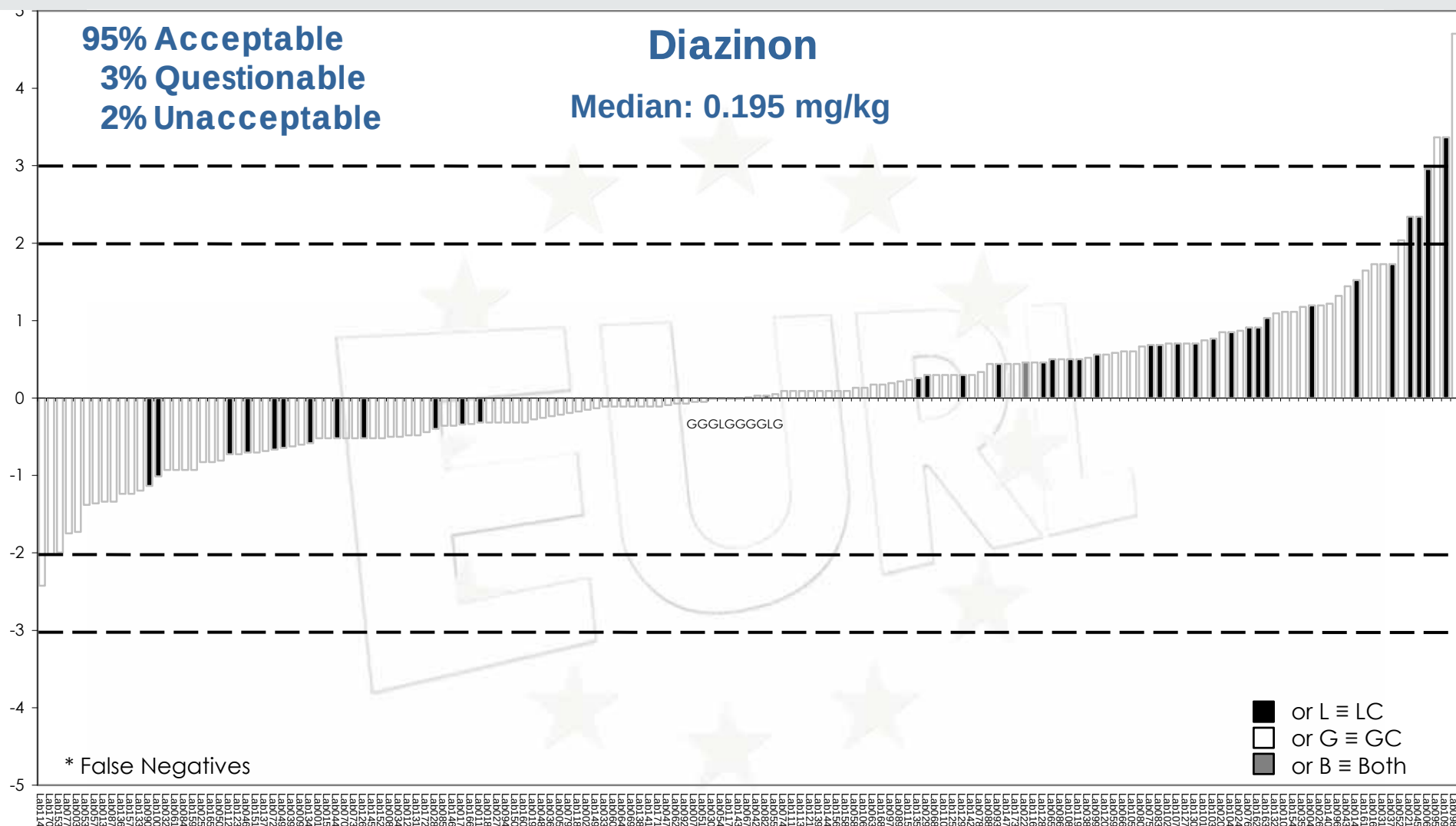


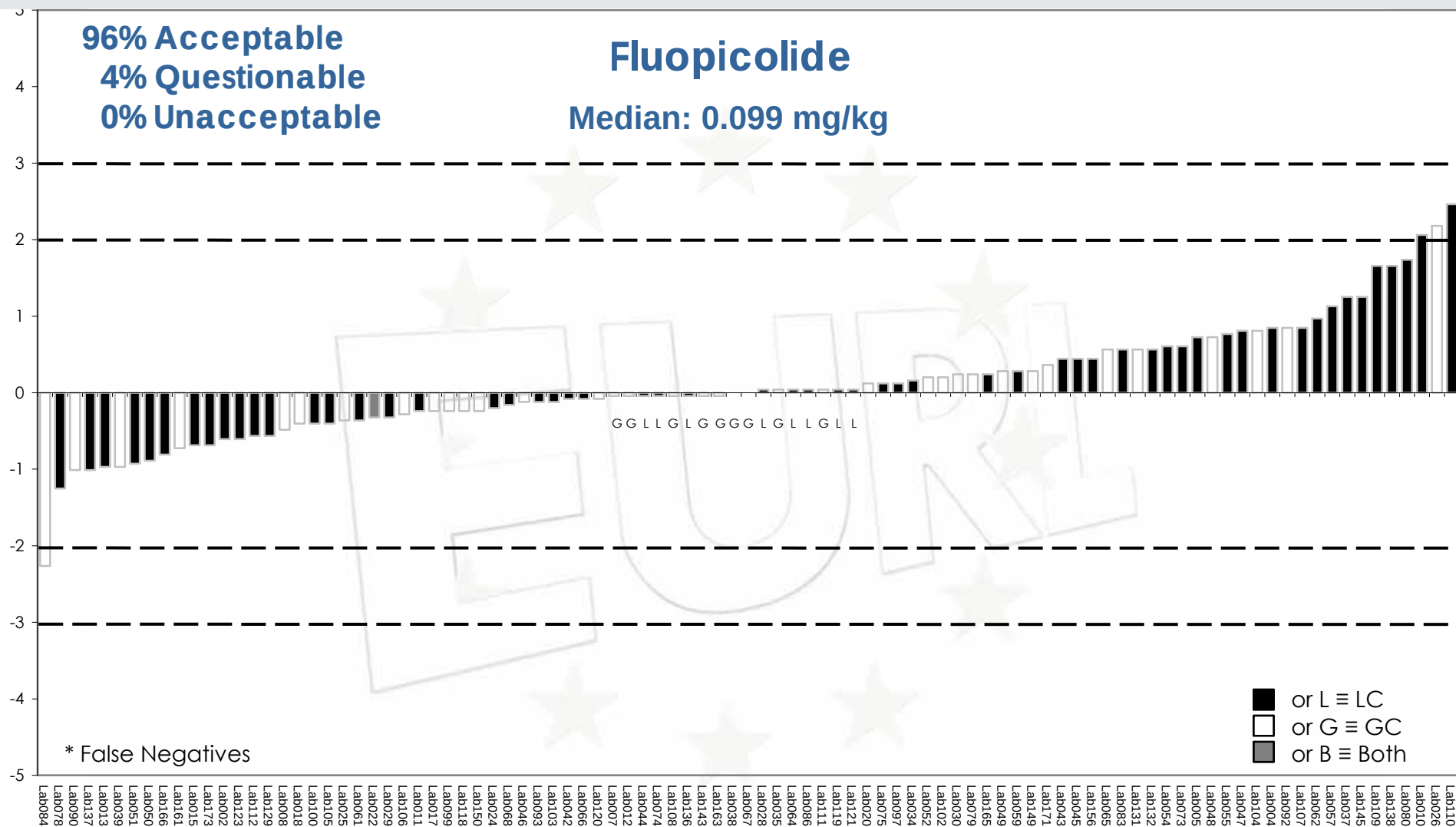


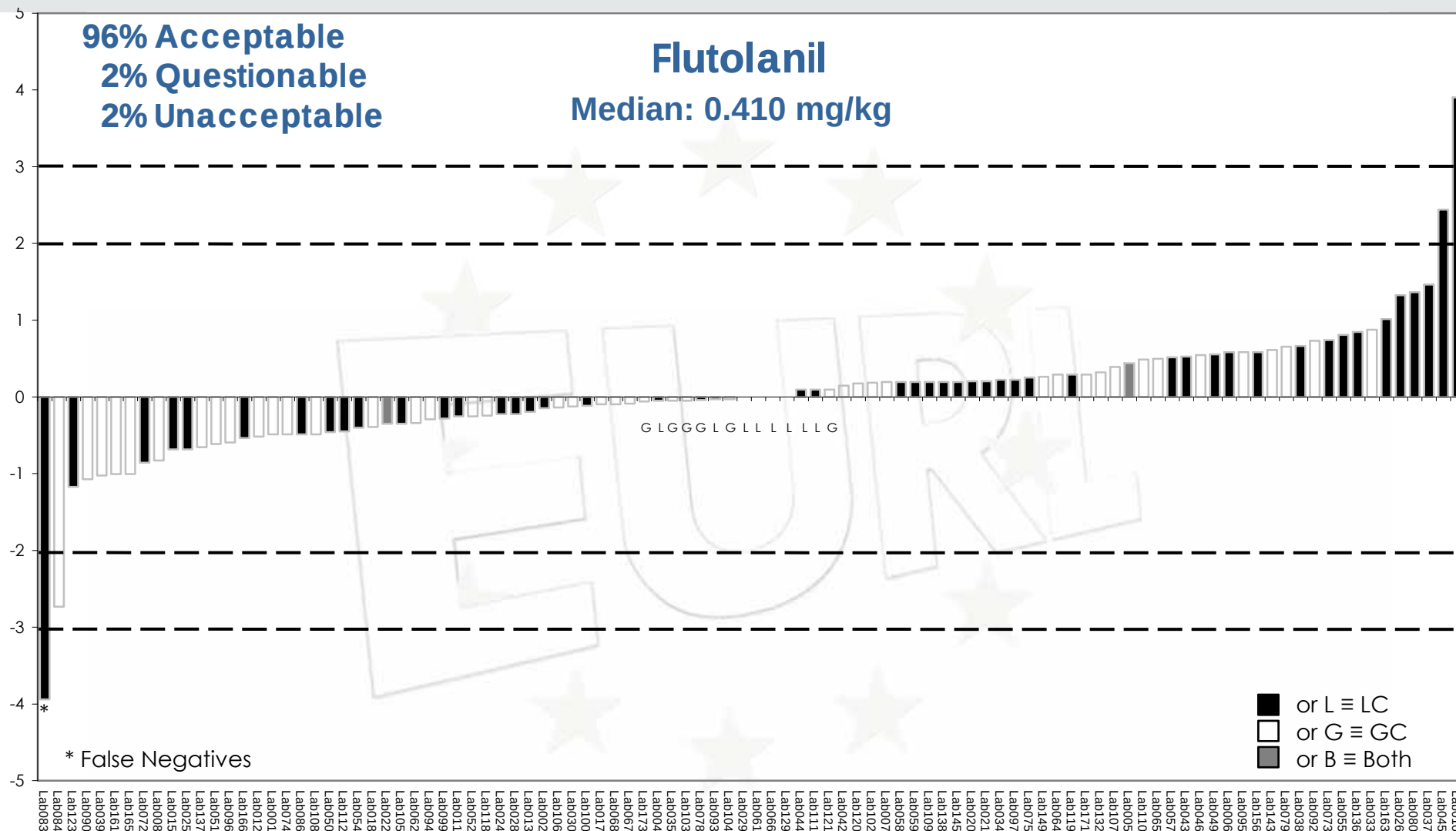


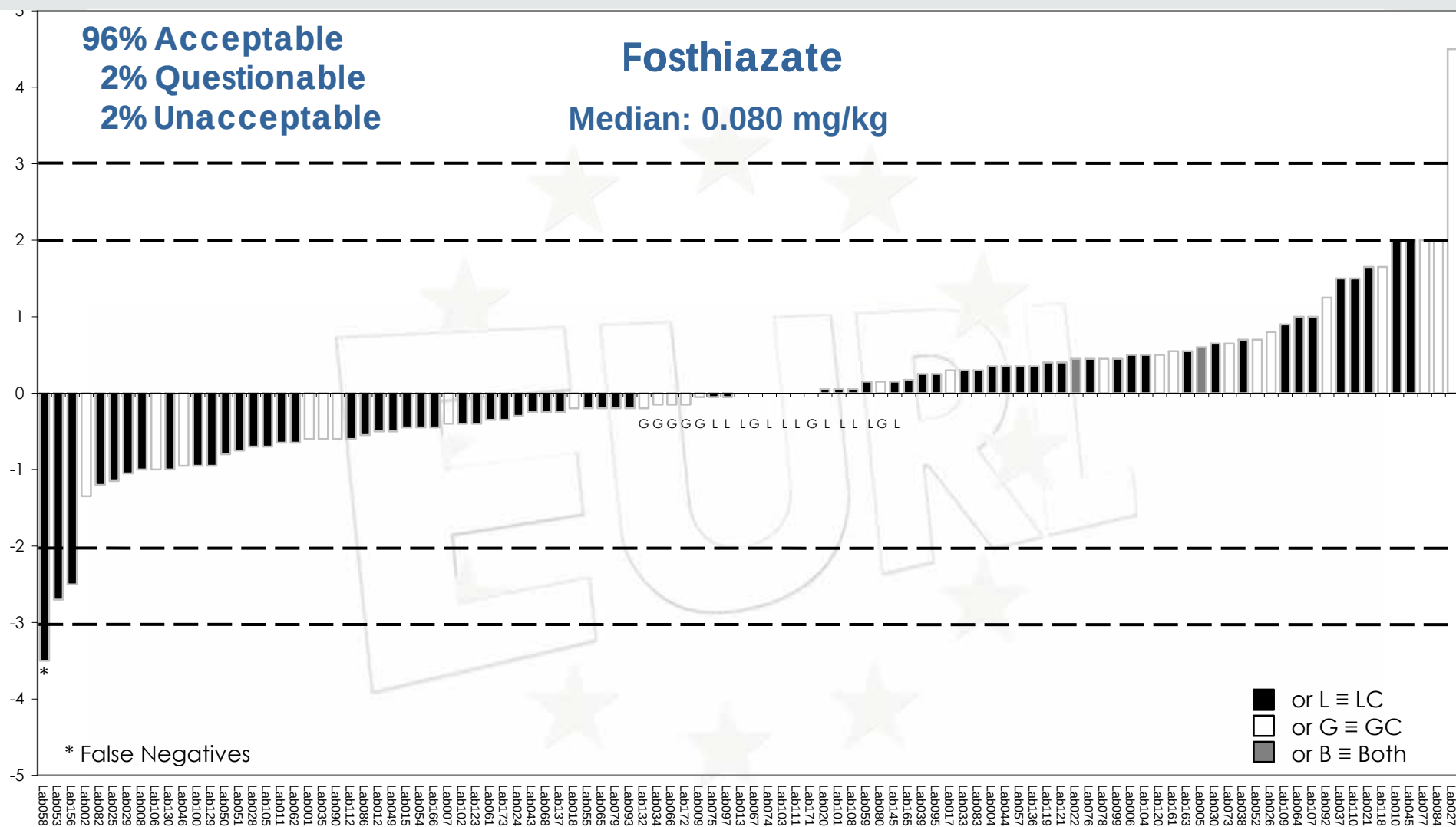


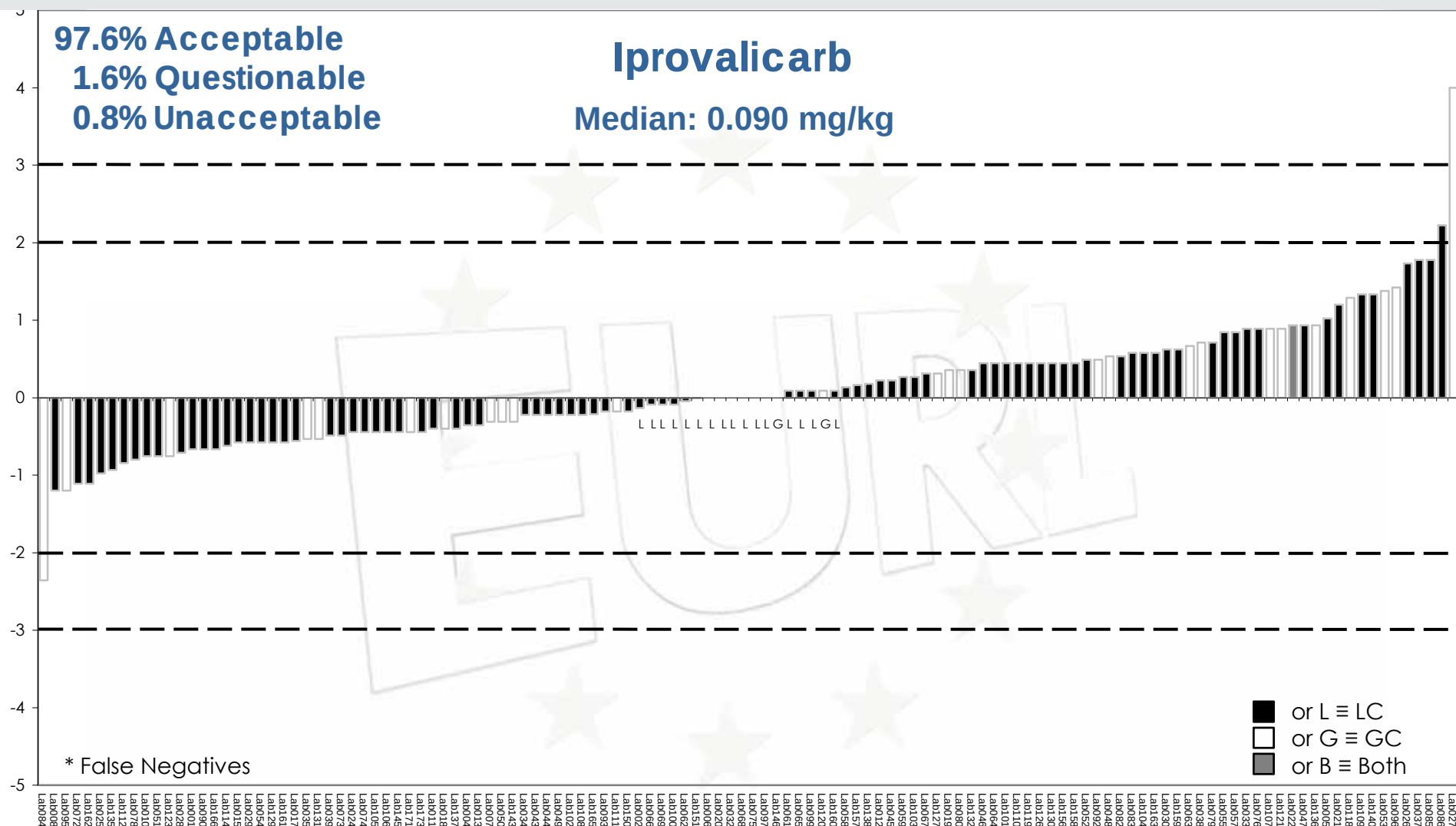


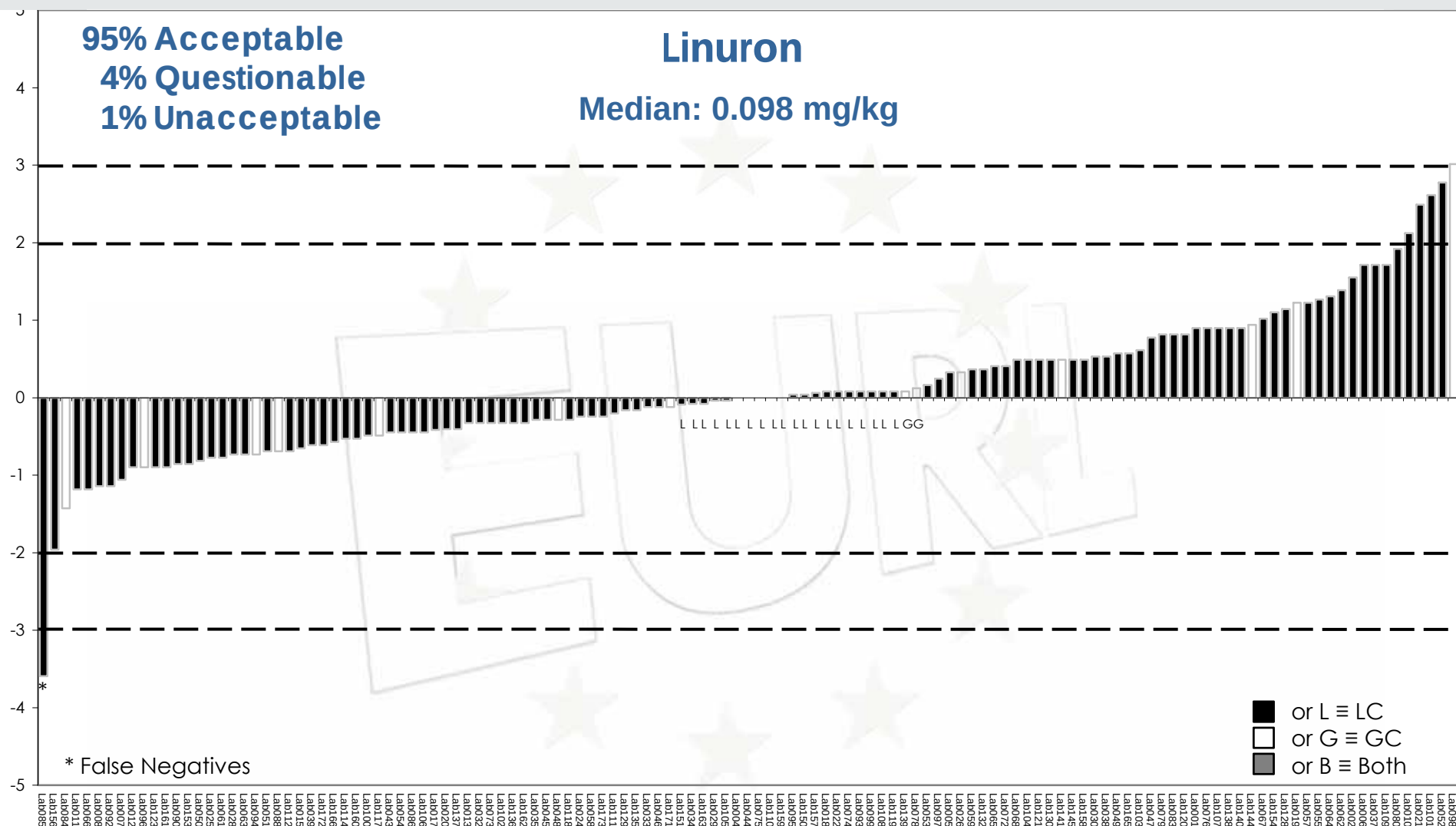


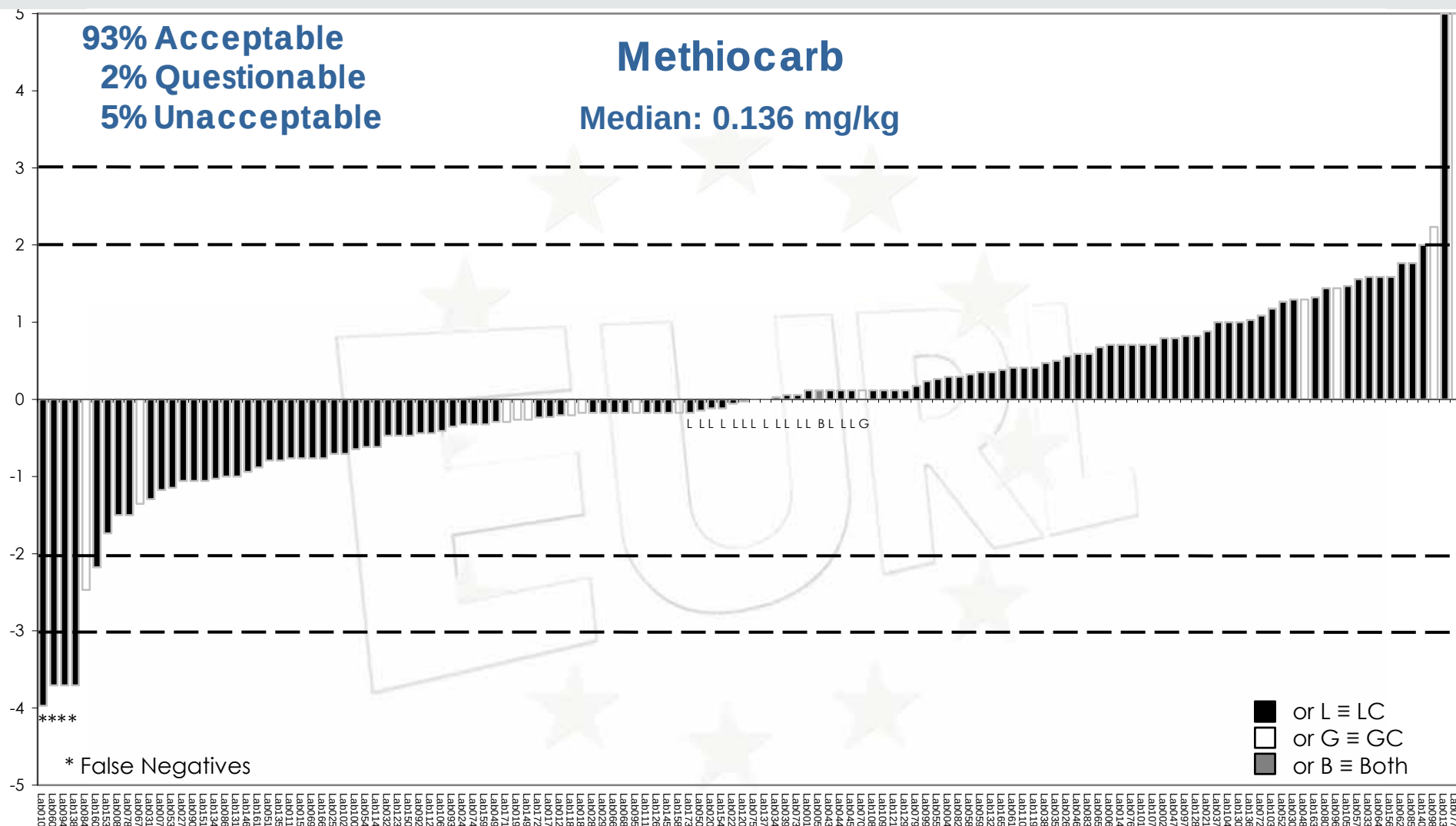


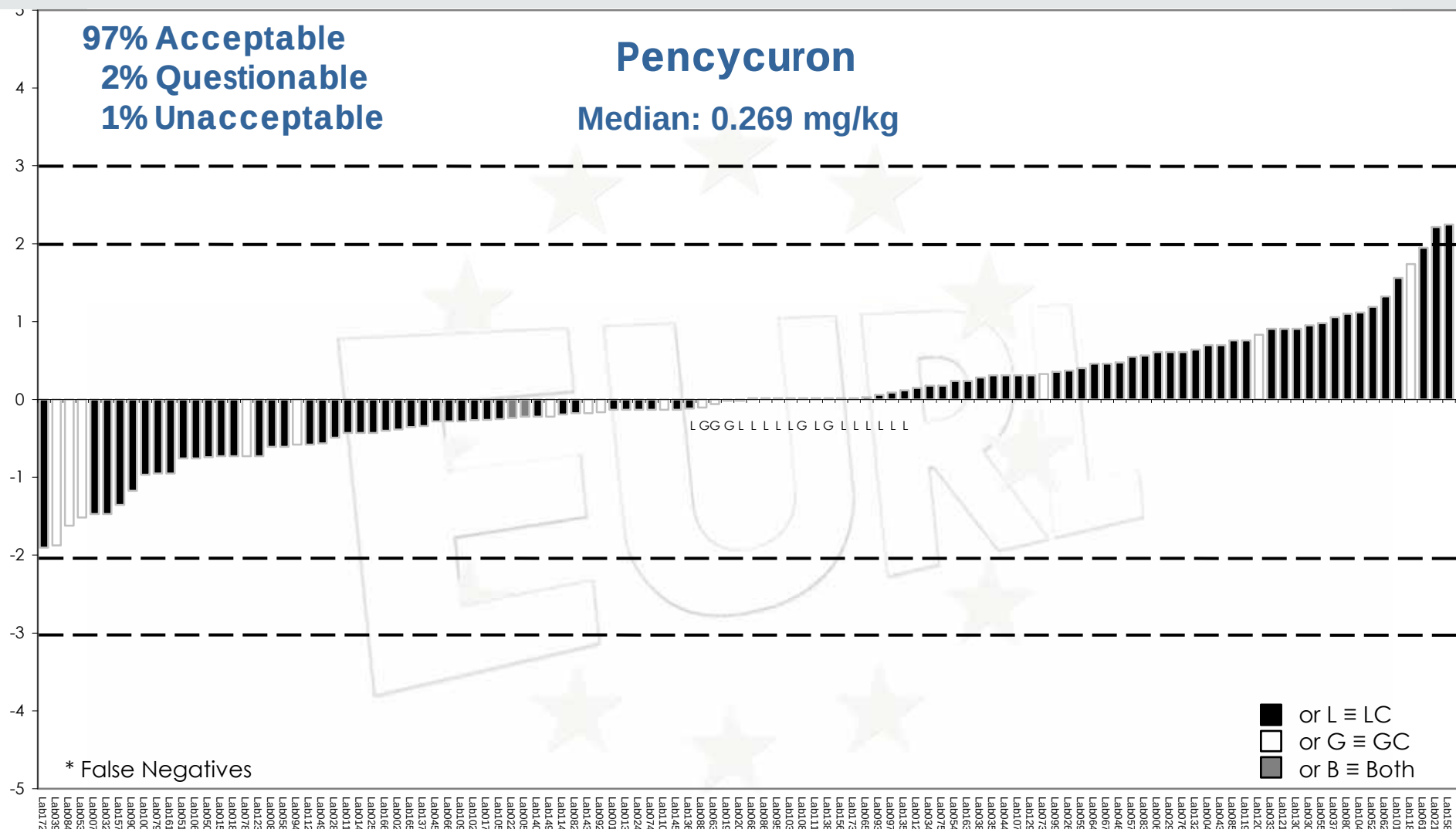


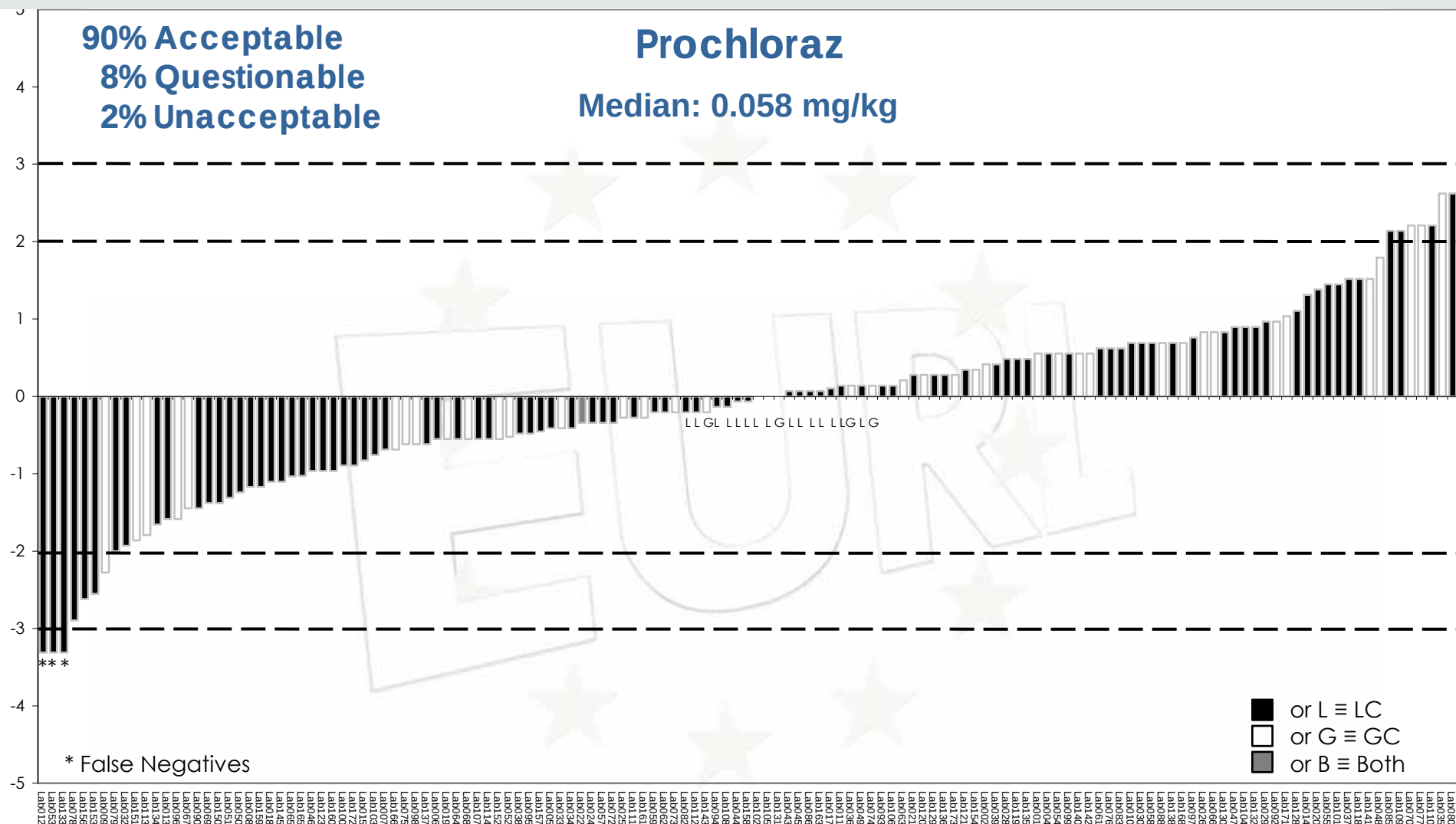


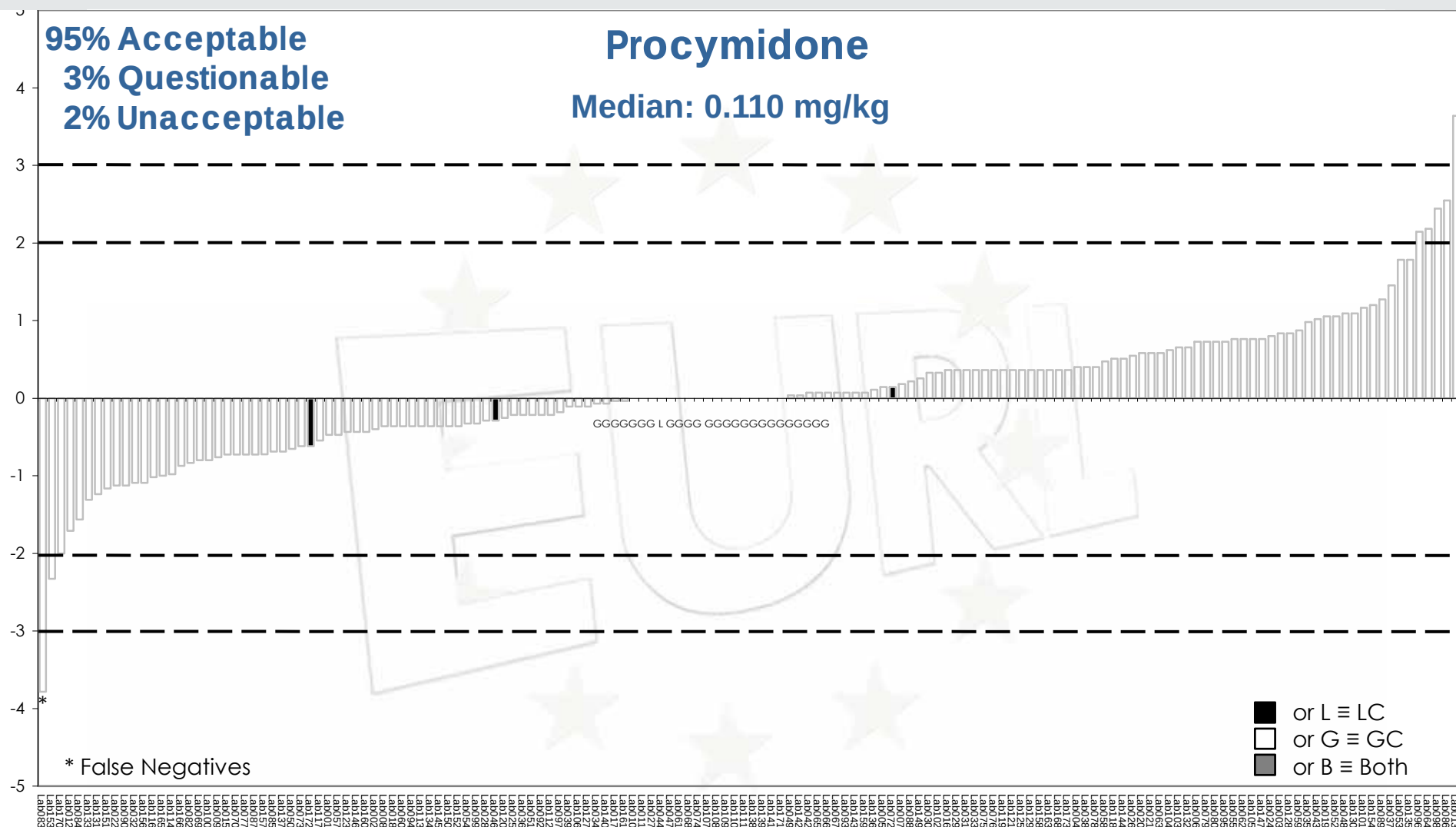


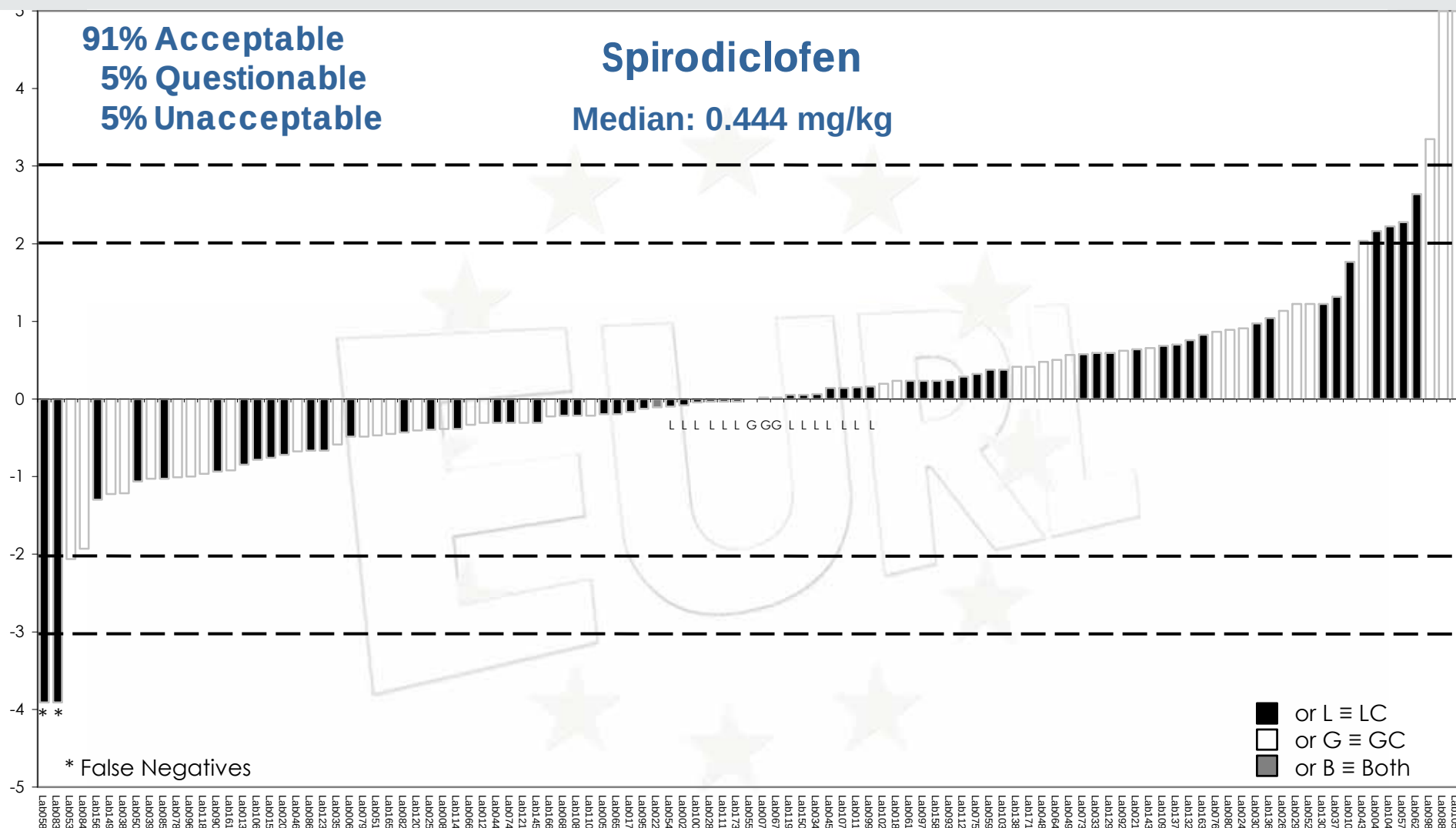


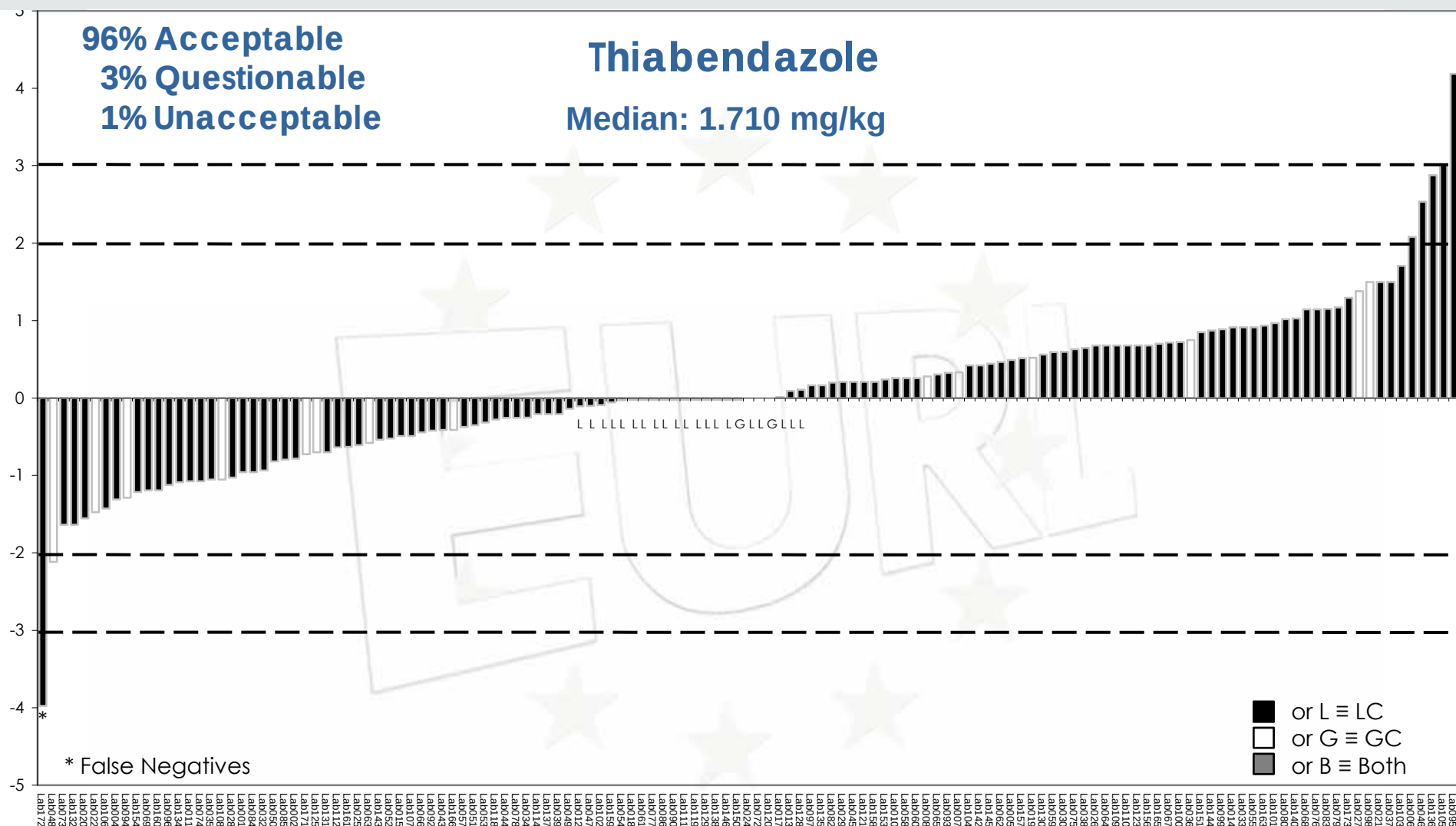


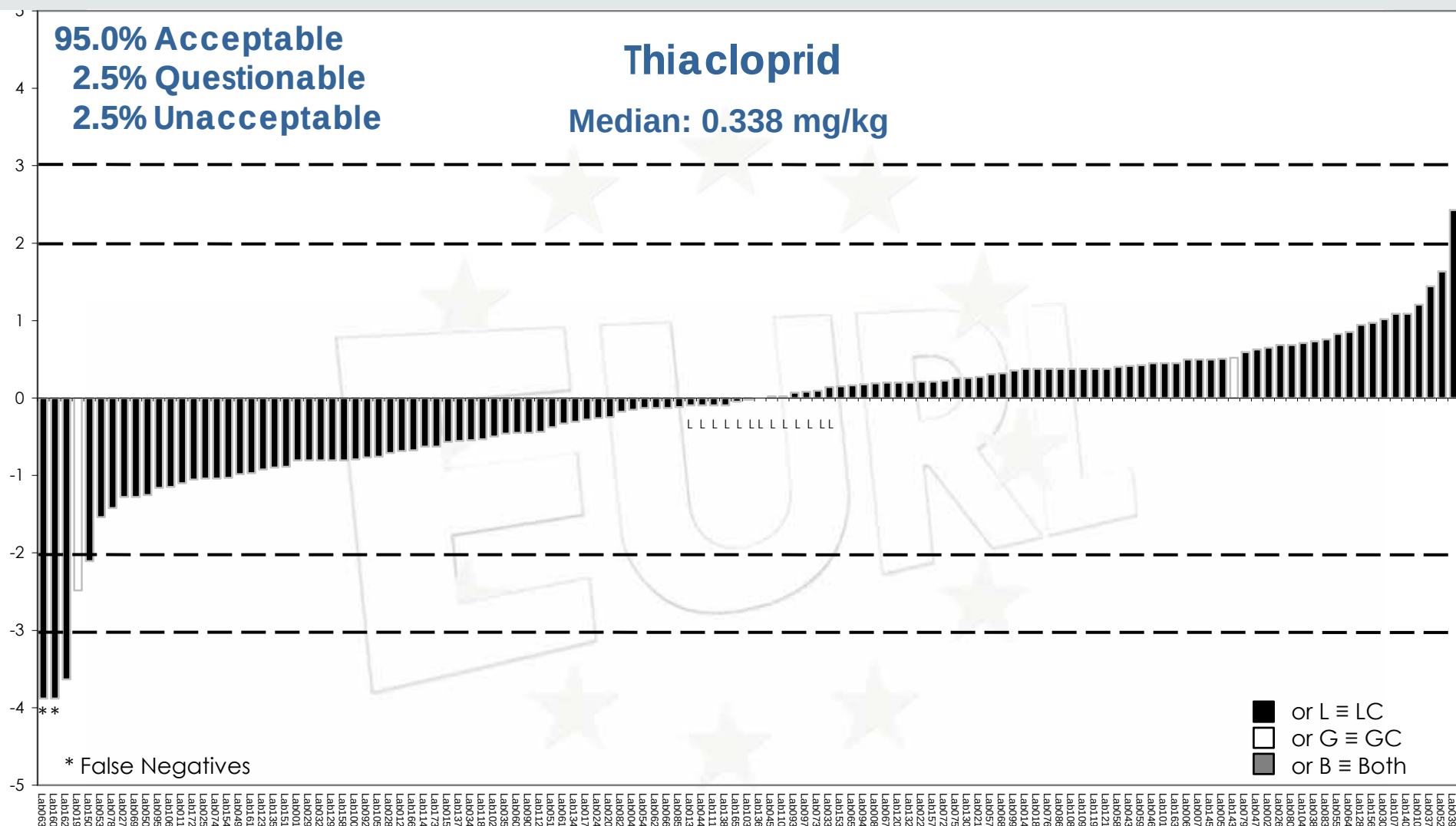












Combined z-Scores

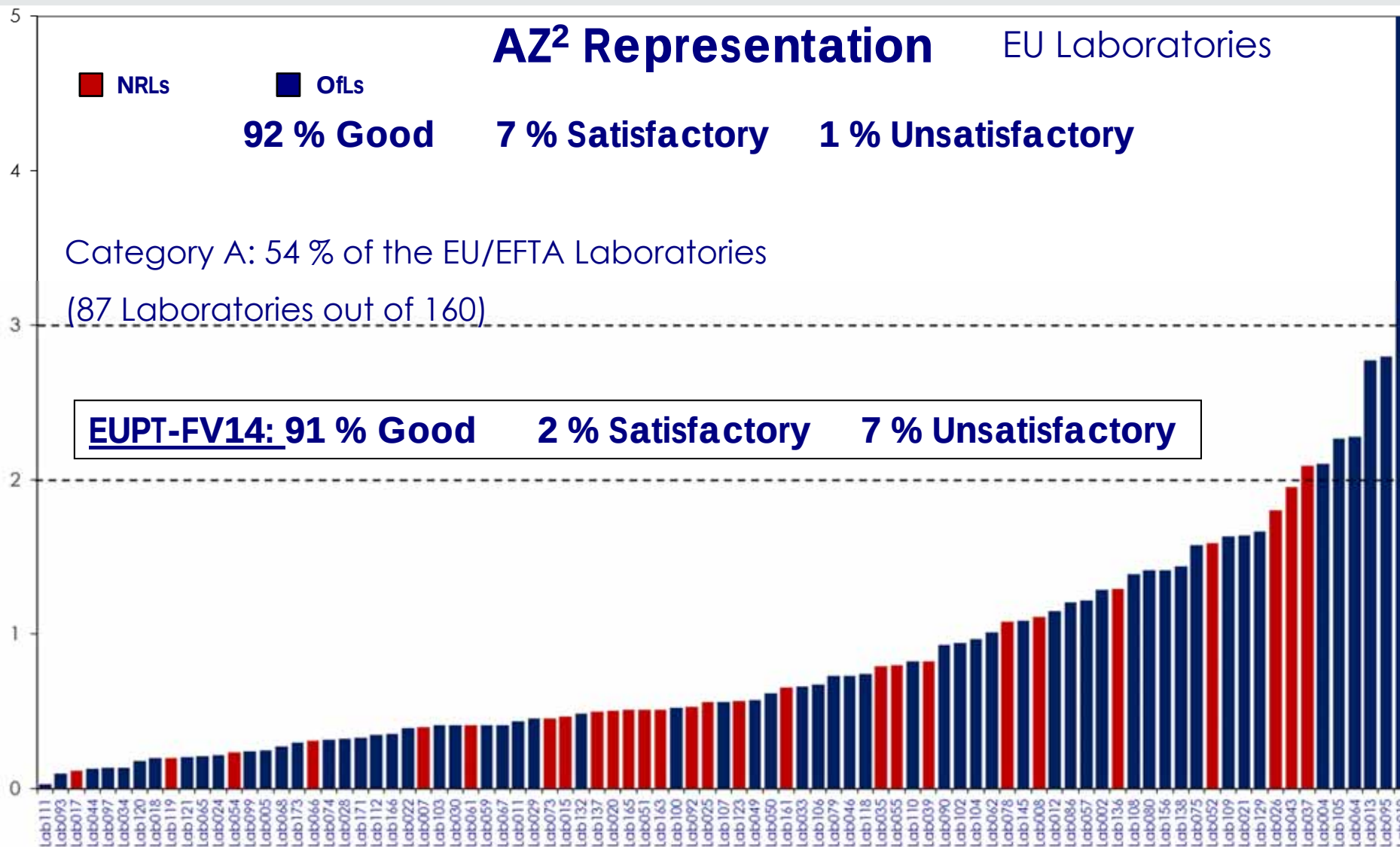
Average of Squared z-Scores

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

$AZ^2 \leq 2$ Good

$2 < AZ^2 \leq 3$ Satisfactory

$AZ^2 > 3$ 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)
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

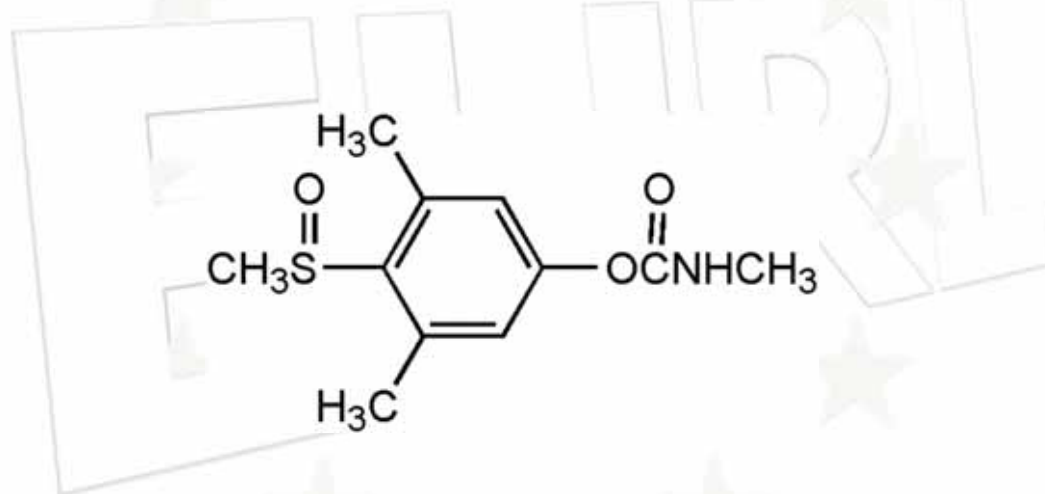
Fludioxonil

Methiocarb sulfone

Tebuconazole

Other detected pesticides

Metabolites

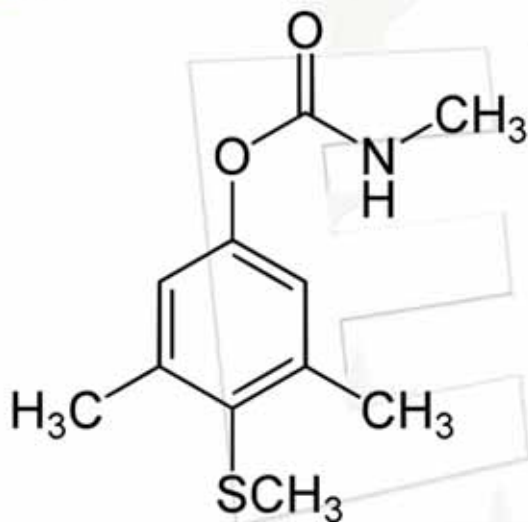


Methiocarb sulfoxide

Other detected pesticides

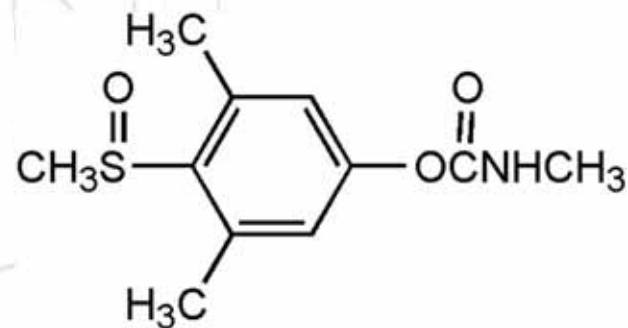


Spiked with methiocarb



Methiocarb

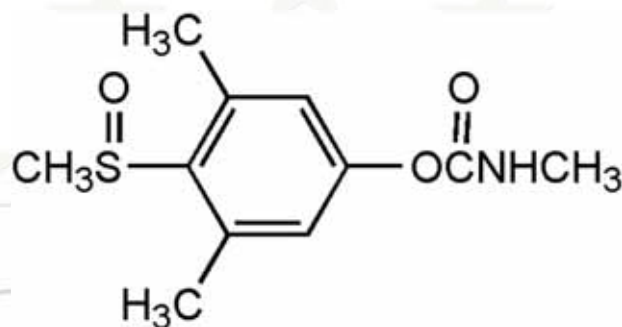
0.136 mg/kg



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

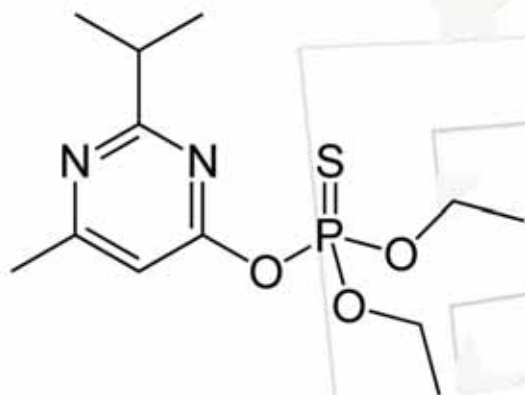
Impurities of commercial formulations



Other detected pesticides

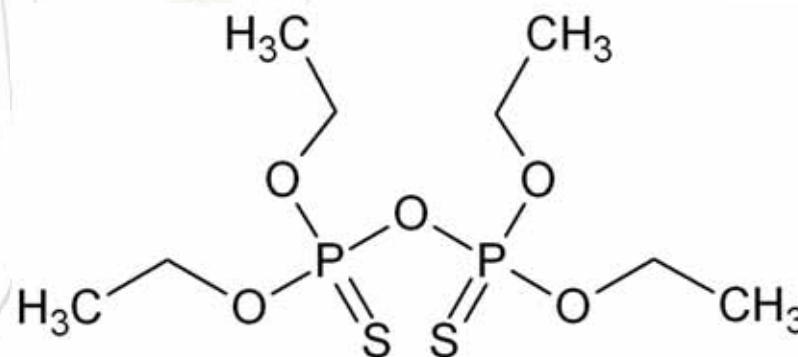


Spiked with diazinon



Diazinon

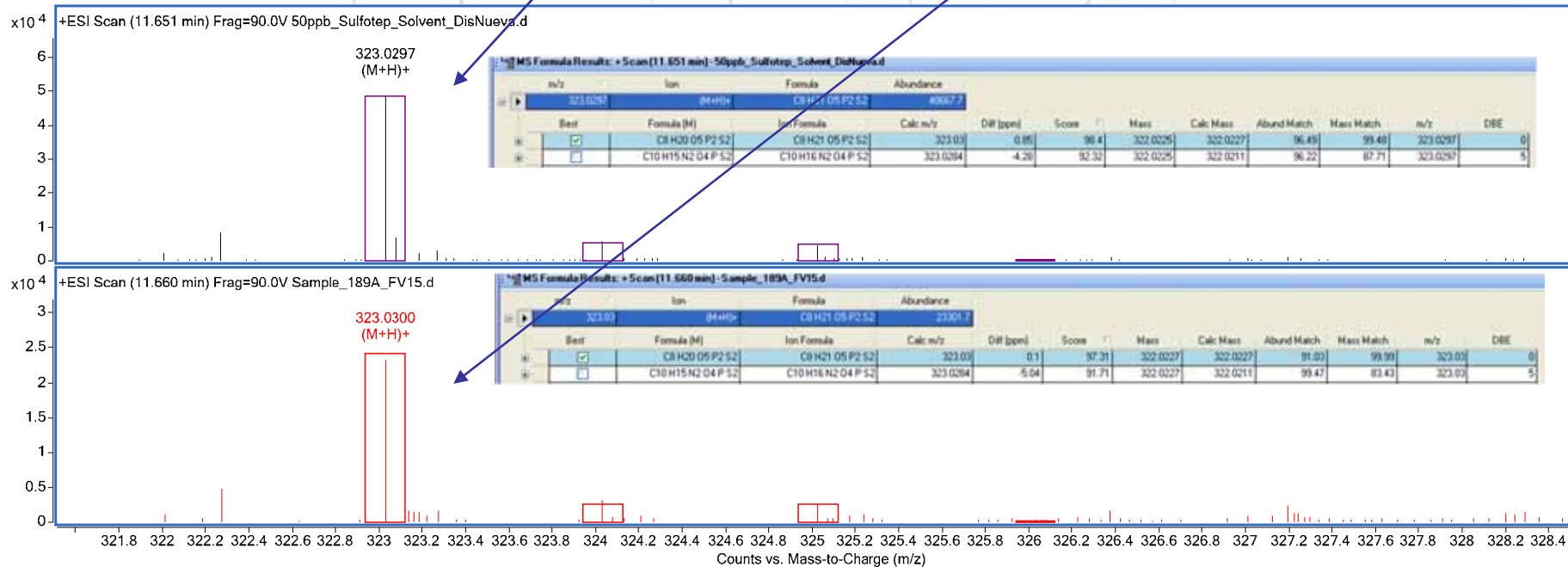
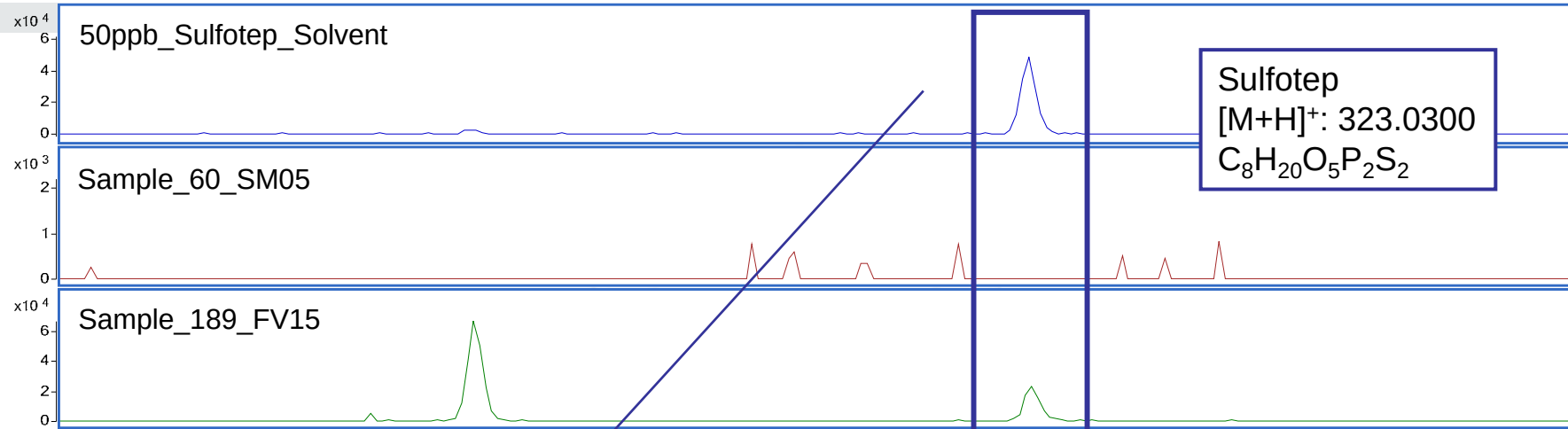
0.195 mg/kg



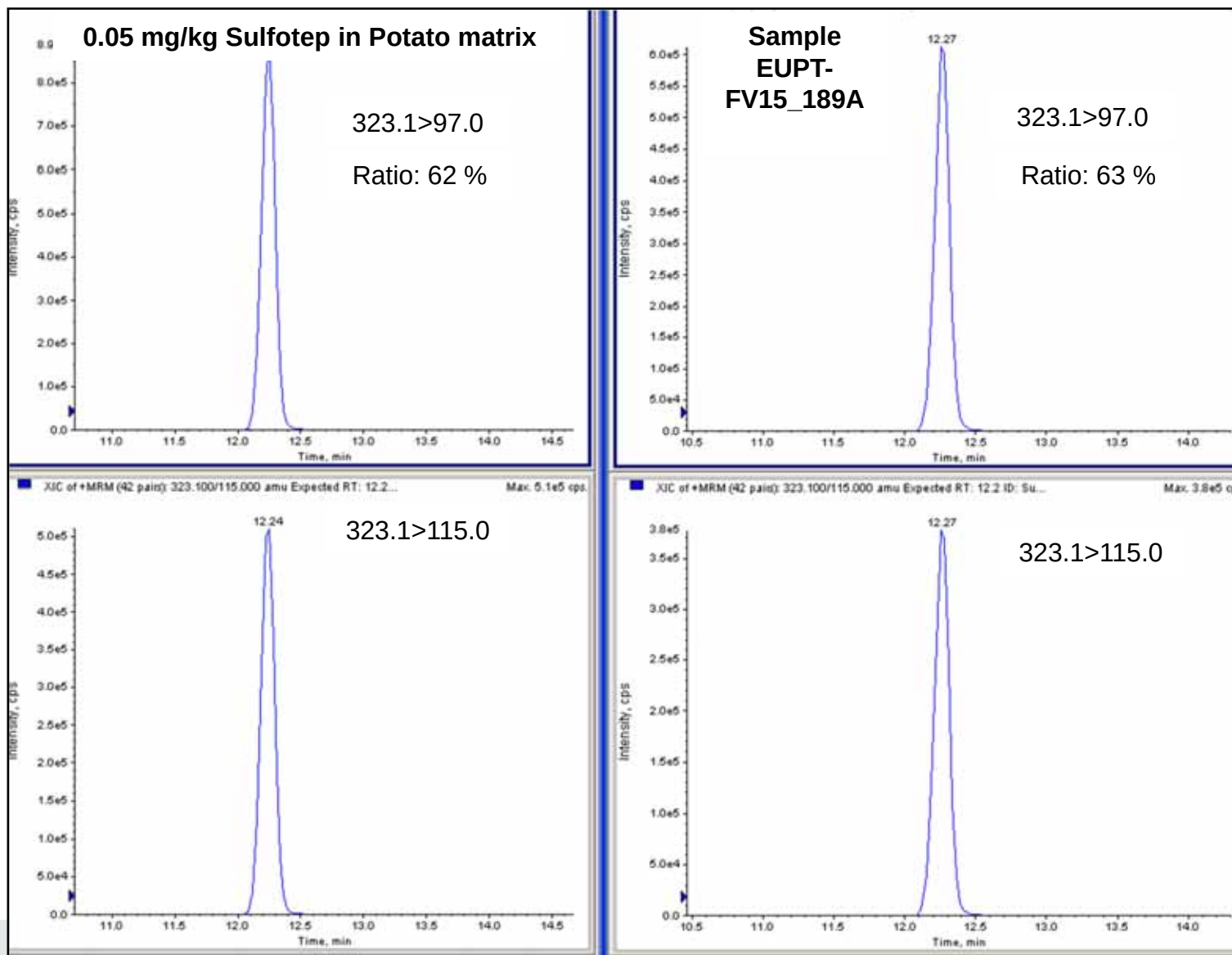
Sulfotep

Aprox. 0.040 mg/kg

(**NOT** included in the target list)



LC-QQQ-MS/MS



Other detected pesticides

Contamination of commercial formulations





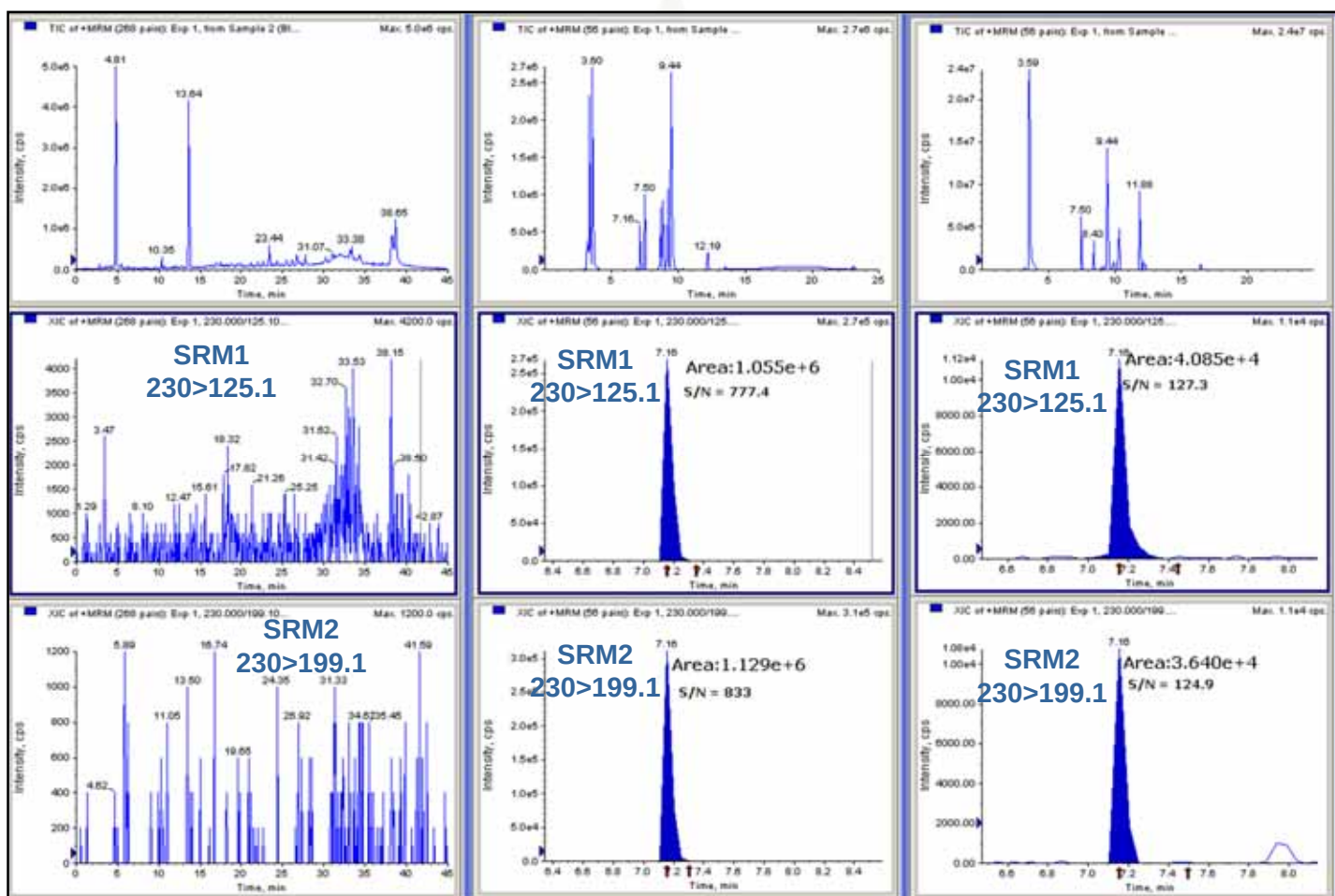
DIMETHOATE

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

BLANK POTATO

Std. 10 µg/kg POTATO

SAMPLE 79A FV15





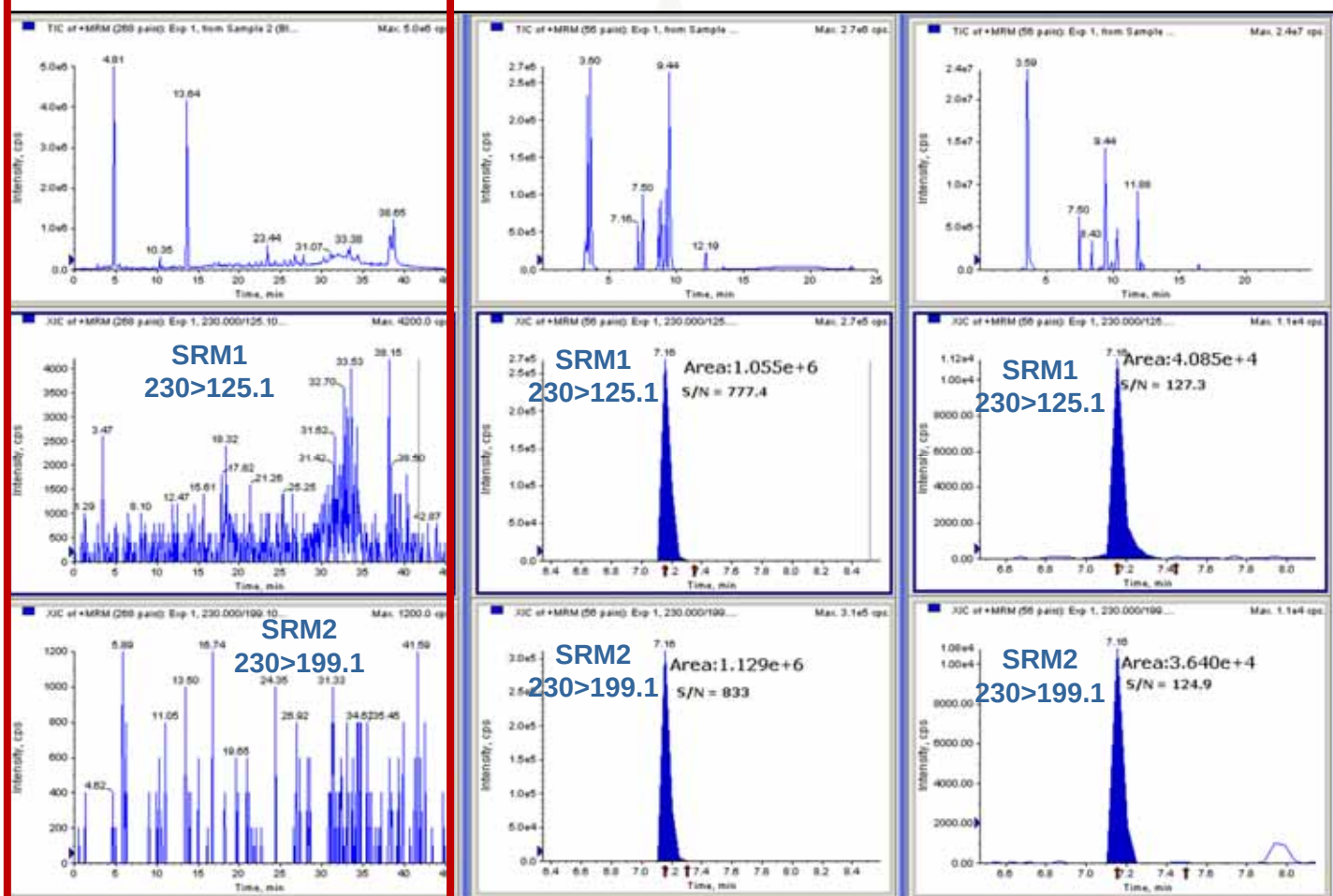
DIMETHOATE

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

BLANK POTATO

Std. 10 µg/kg POTATO

SAMPLE 79A FV15

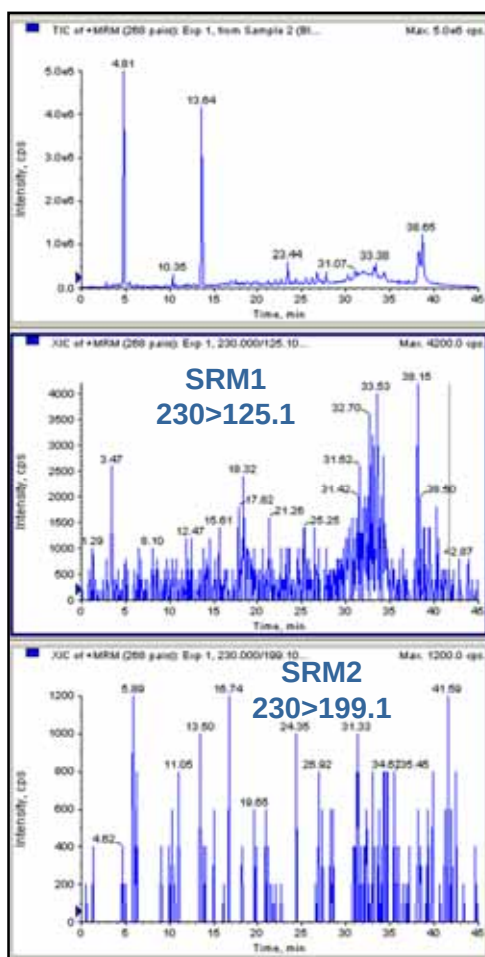




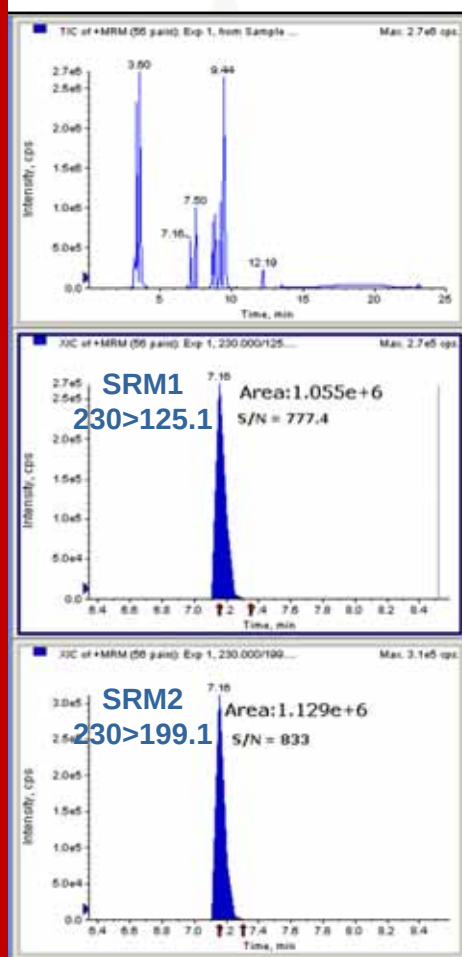
DIMETHOATE

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

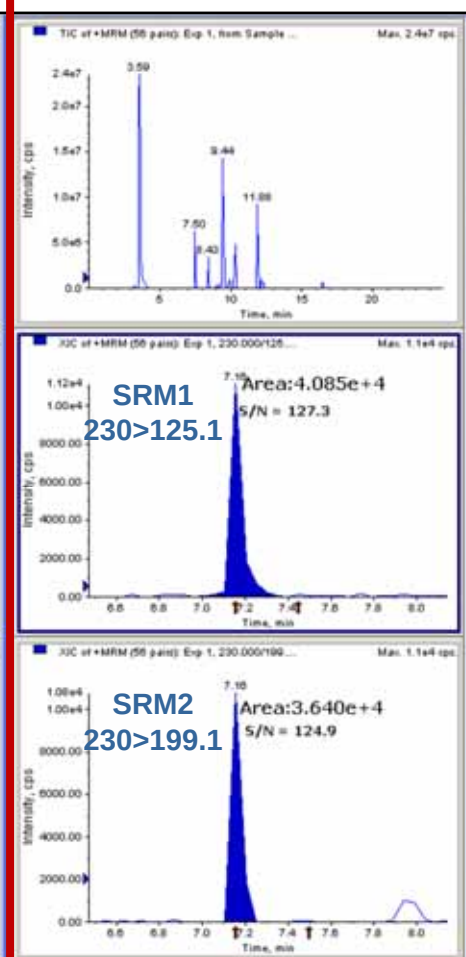
BLANK POTATO



Std. 10 µg/kg POTATO



SAMPLE 79A FV15





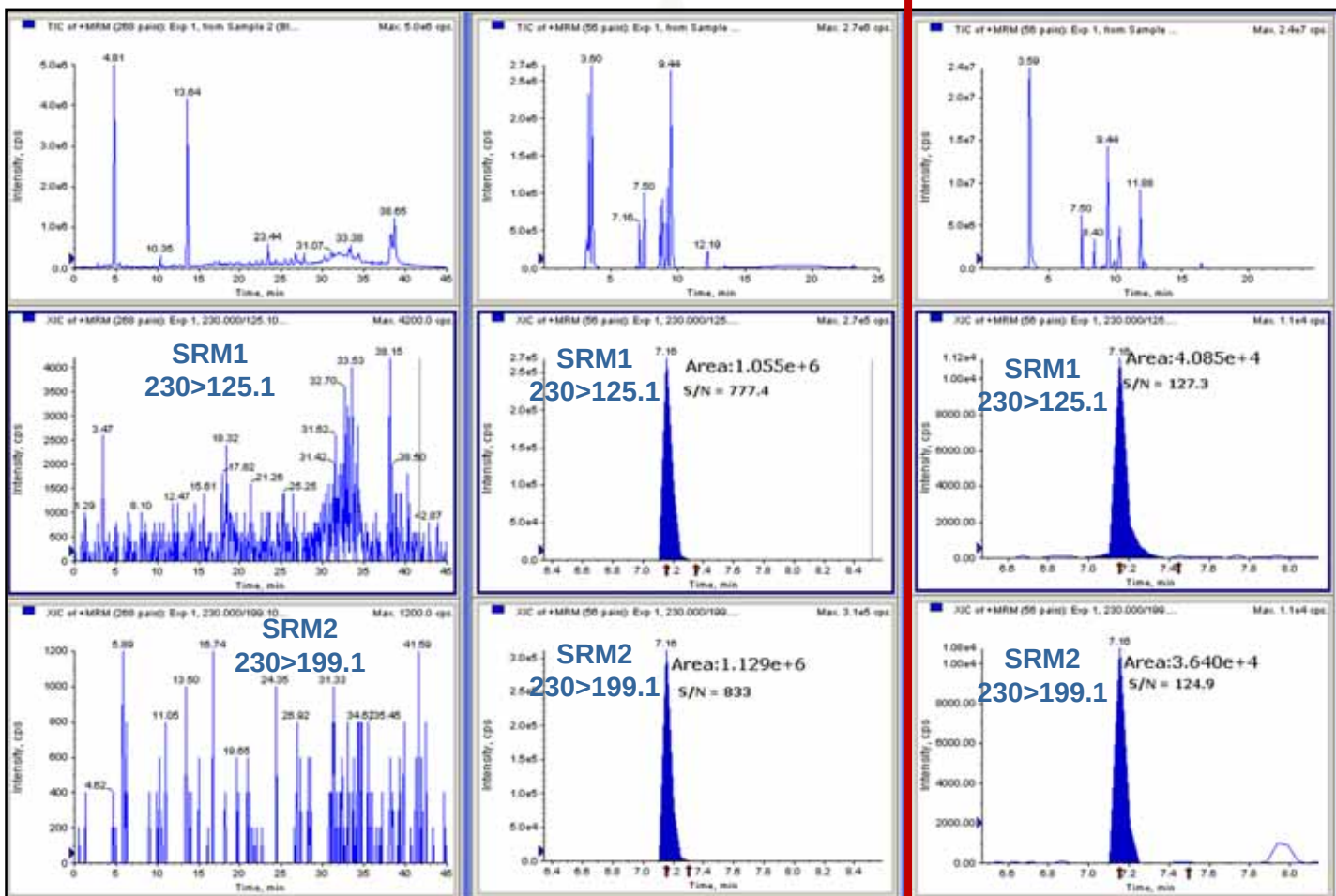
DIMETHOATE

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

BLANK POTATO

Std. 10 µg/kg POTATO

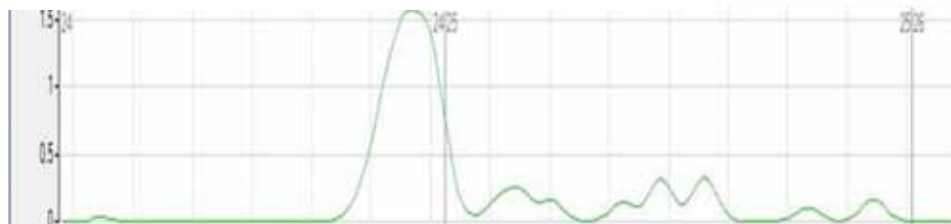
SAMPLE 79A FV15



Endosulfan Alpha (concentration < 10 µg/kg)

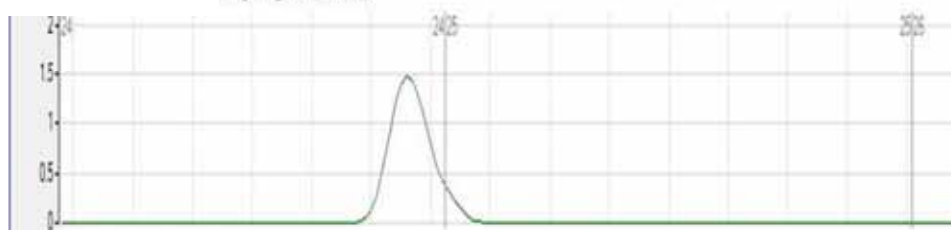
238.8>204

Std. 5 µg/kg Potato

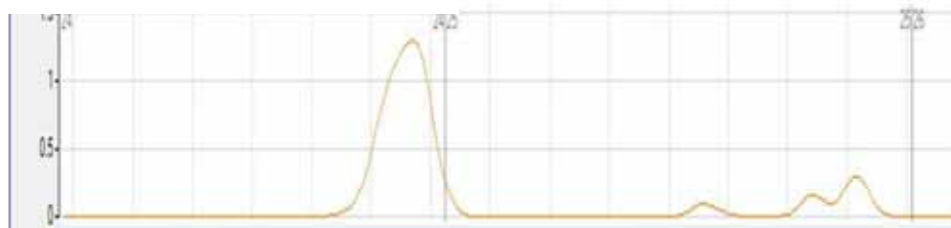


241>206

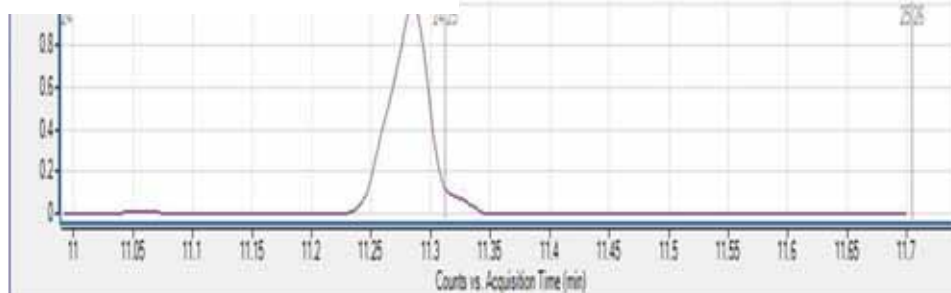
iABC_Potato_Quechers.D Smooth



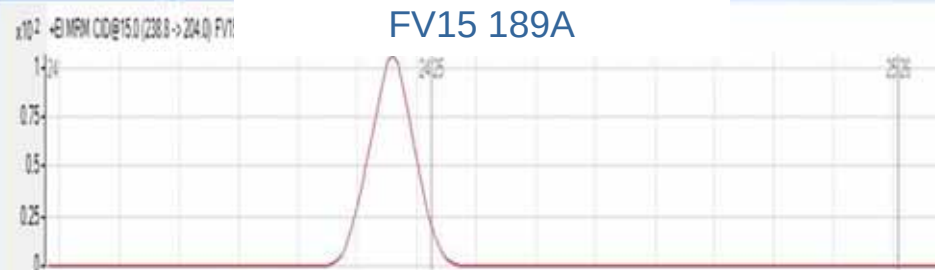
194.9>158



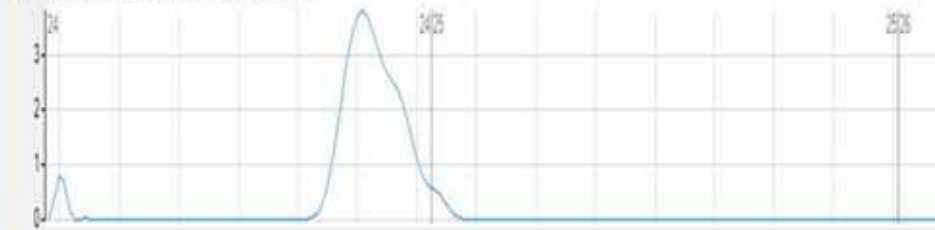
194.9>160



FV15 189A



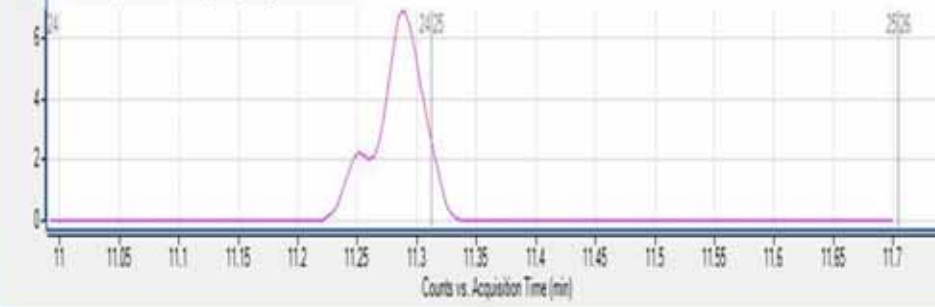
x10⁻¹ -E1 MRM (241.0->206.0) FV15_189A_Quechers.D Smooth



x10⁻¹ -E1 EIC MRM (195.0, 194.9->160.0) FV15_189A_Quechers.D Smooth



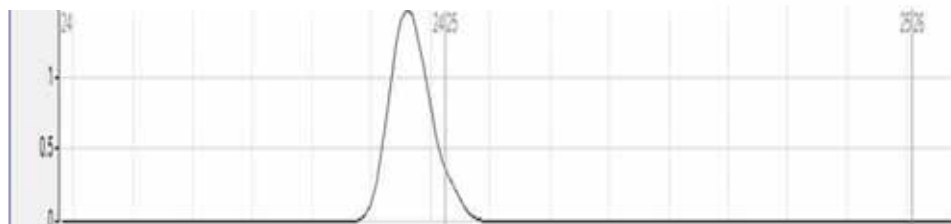
x10⁻¹ -E1 EIC MRM (195.0, 194.9->160.0) FV15_189A_Quechers.D Smooth



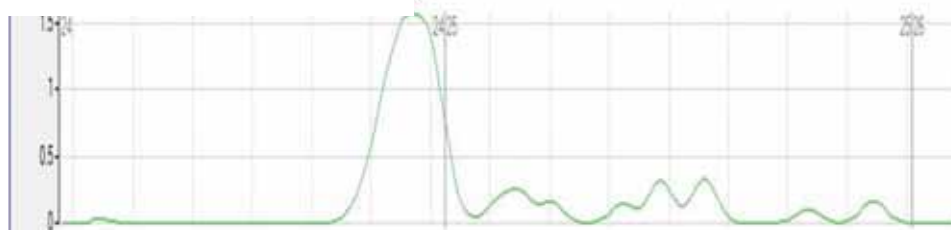
Endosulfan Beta (concentration < 10 µg/kg)

241>206

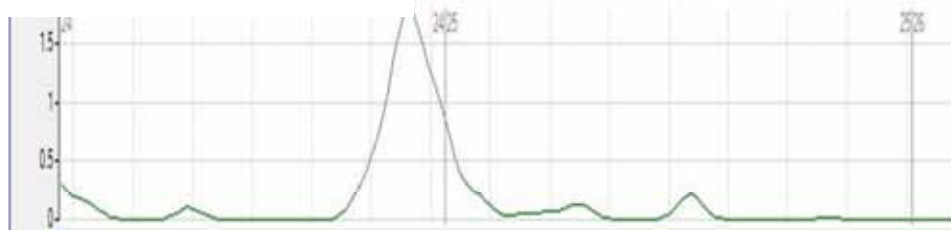
Std. 5 µg/kg Potato



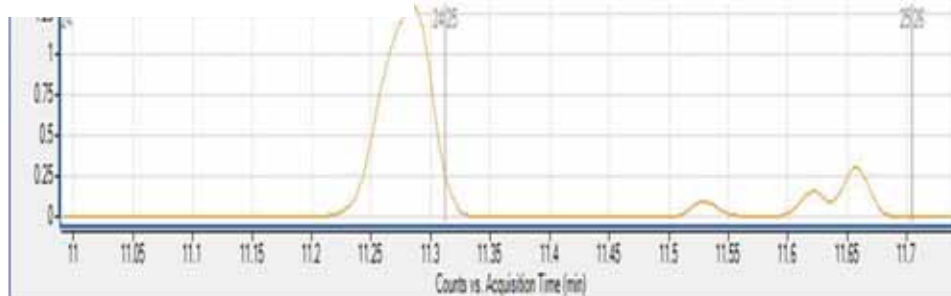
238.8>204



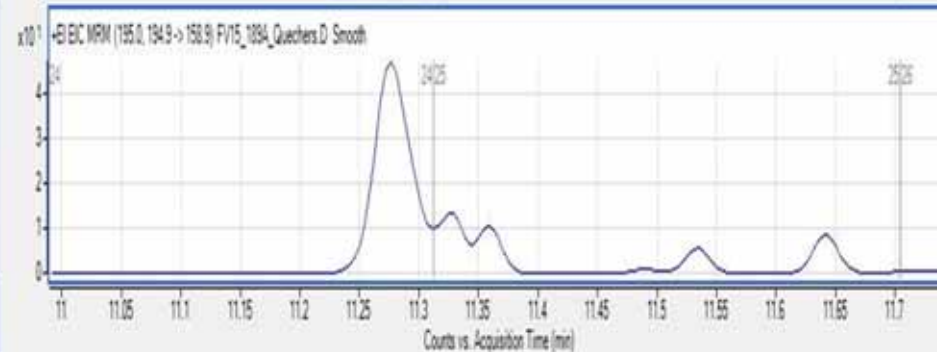
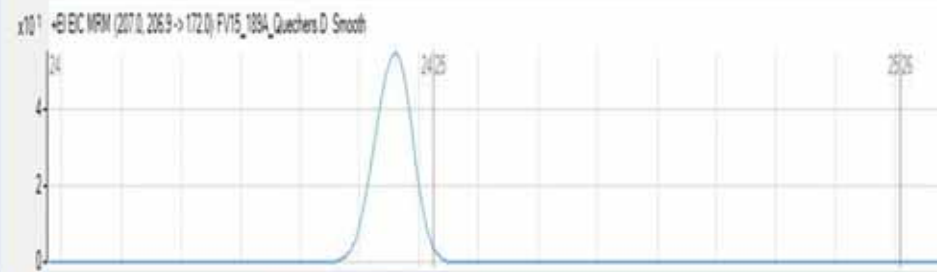
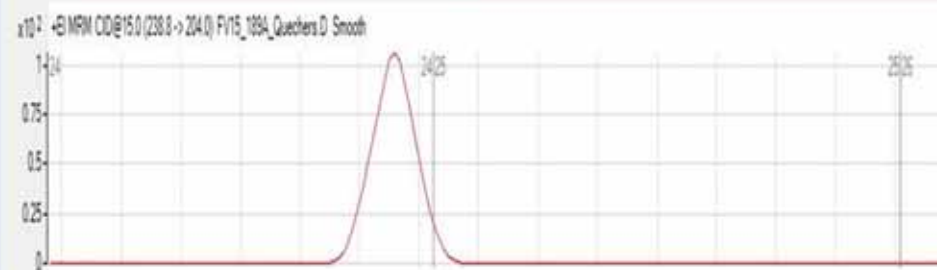
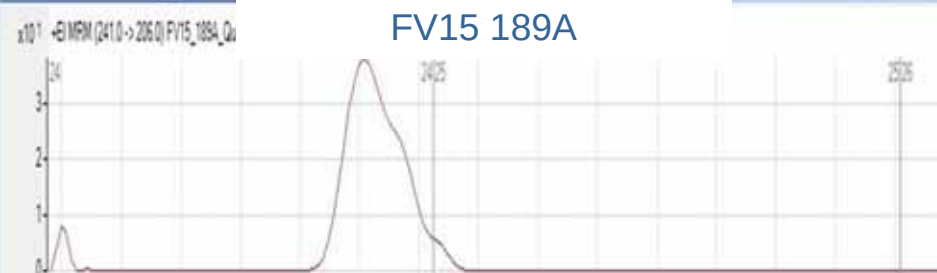
206.9>172



194.9>158.9



FV15 189A





EURL

European Union Reference Laboratory for Pesticide Residues in Fruits & Vegetables

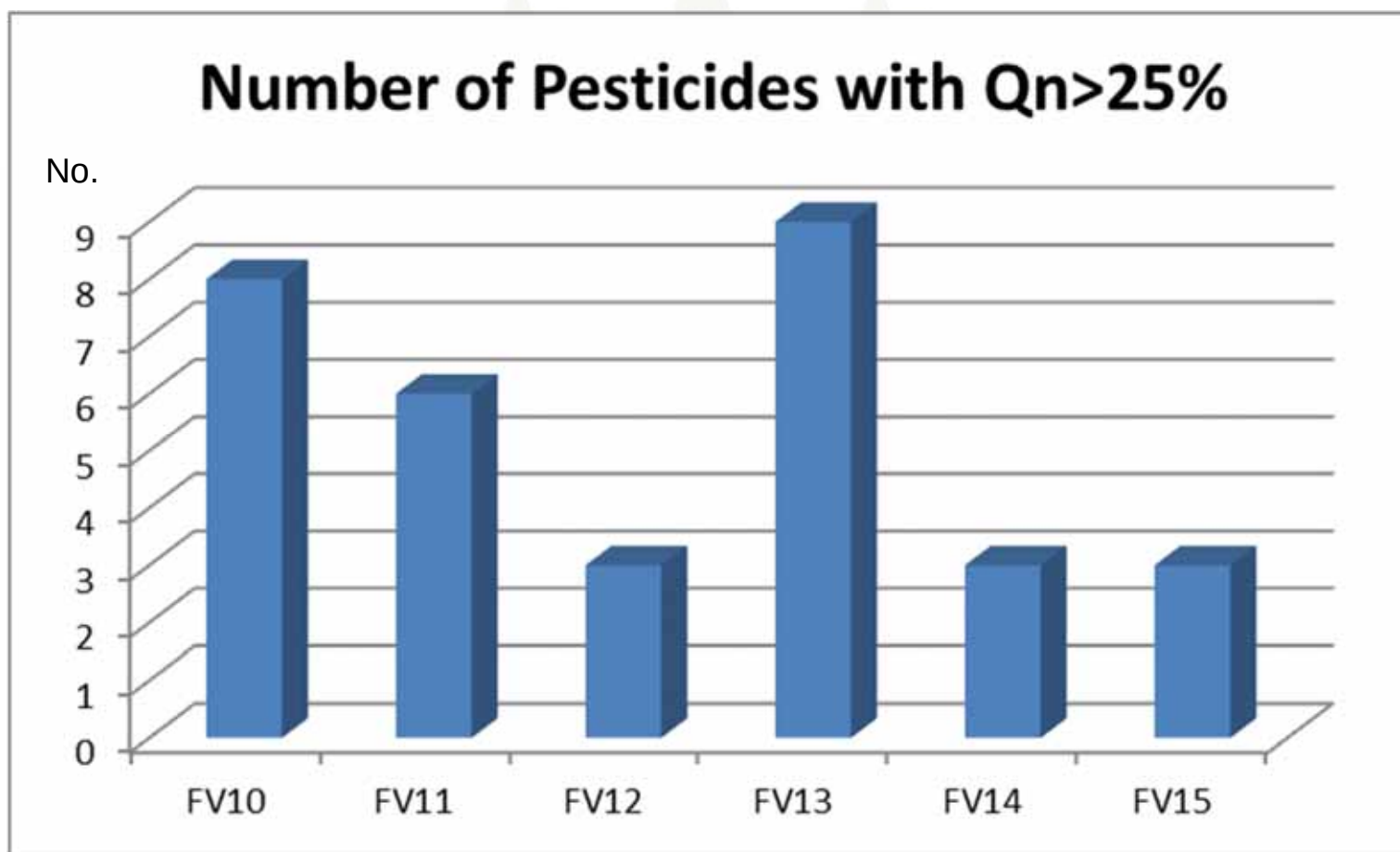
EUPT-FV-15

European Proficiency Test FV-15



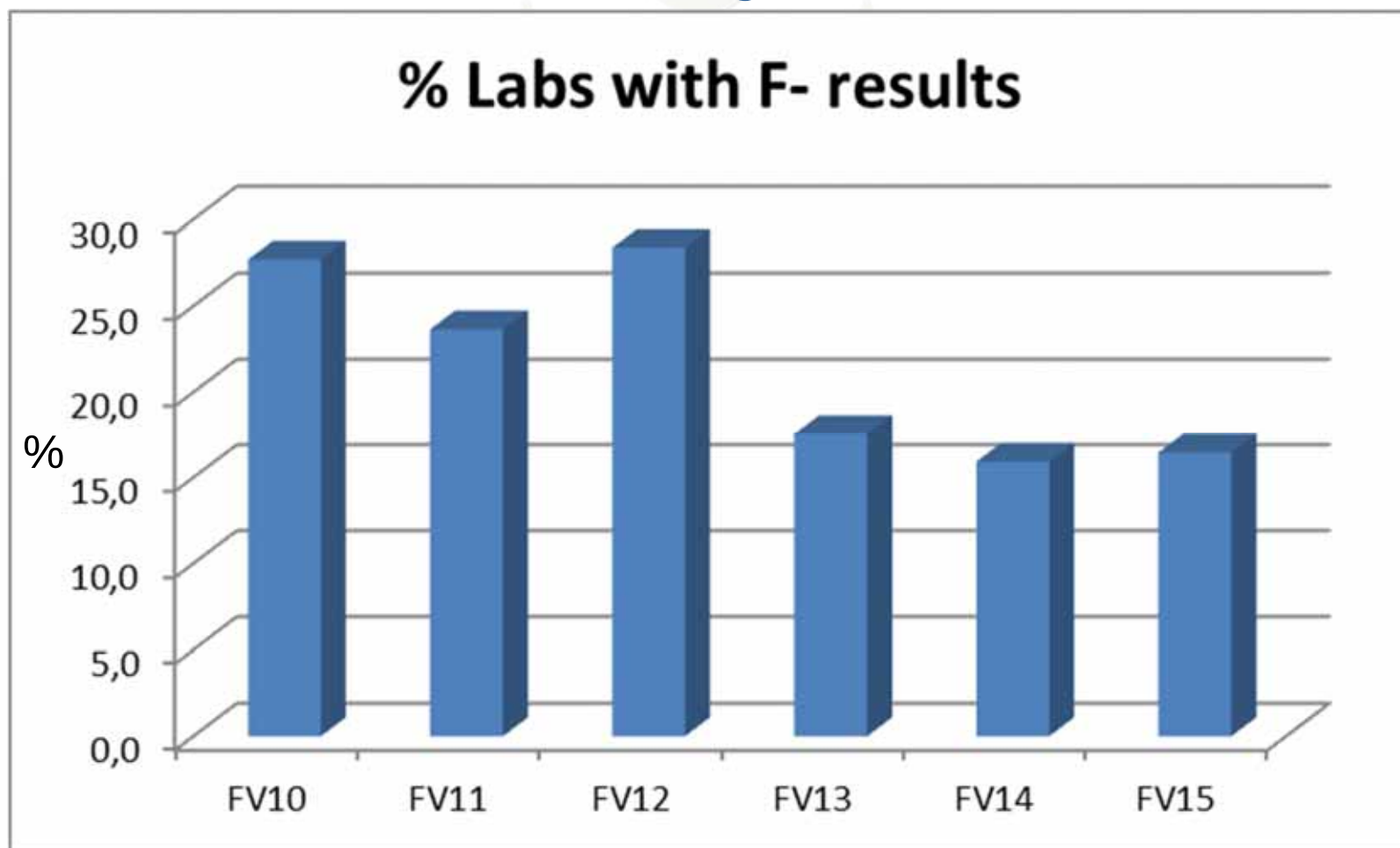
Evolution of the laboratories performance throughout the years

Dispersion of results



Evolution of the laboratories performance throughout the years

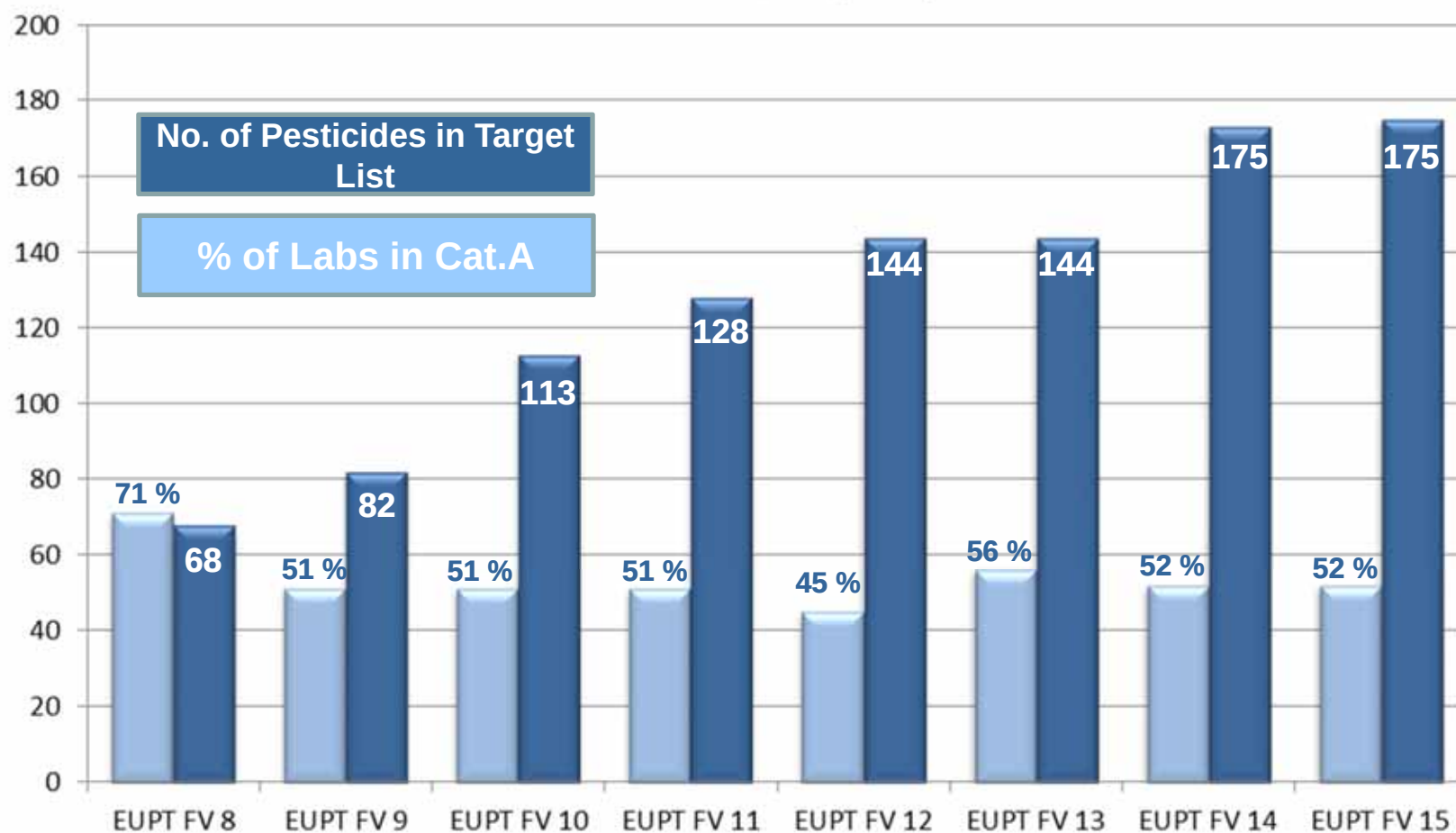
False Negatives





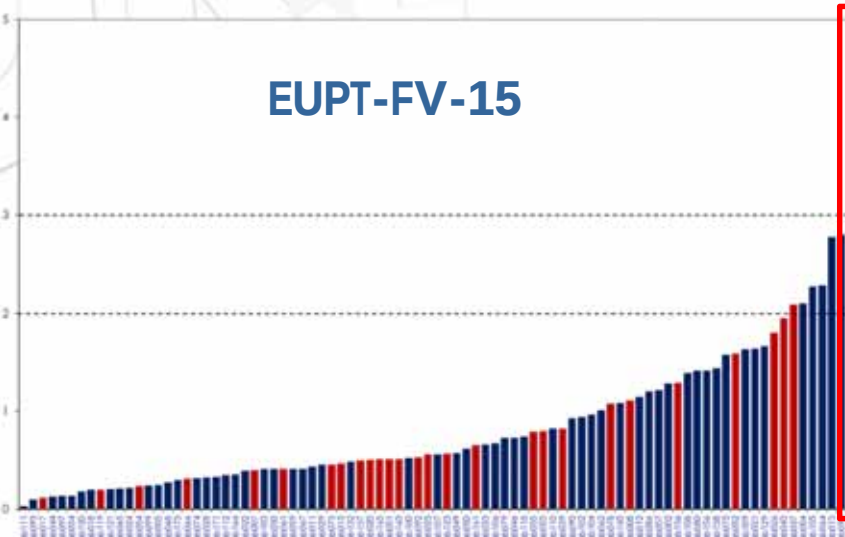
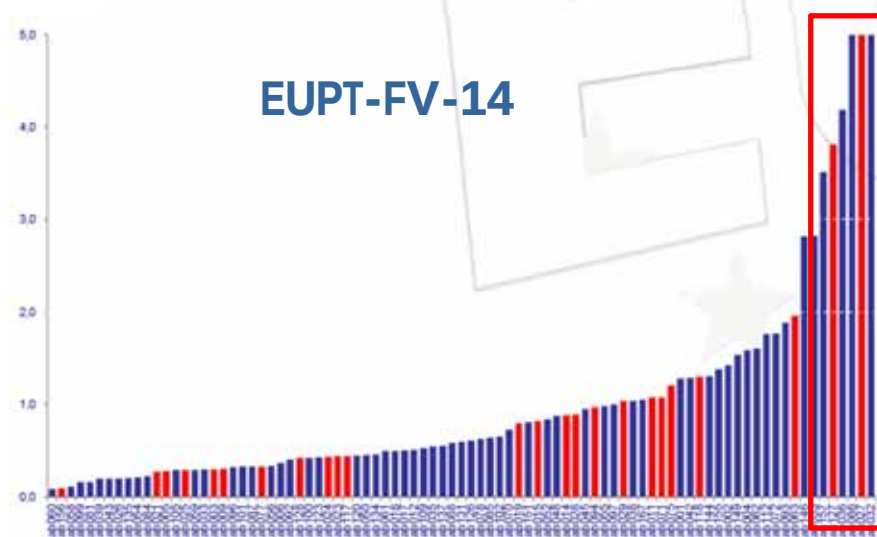
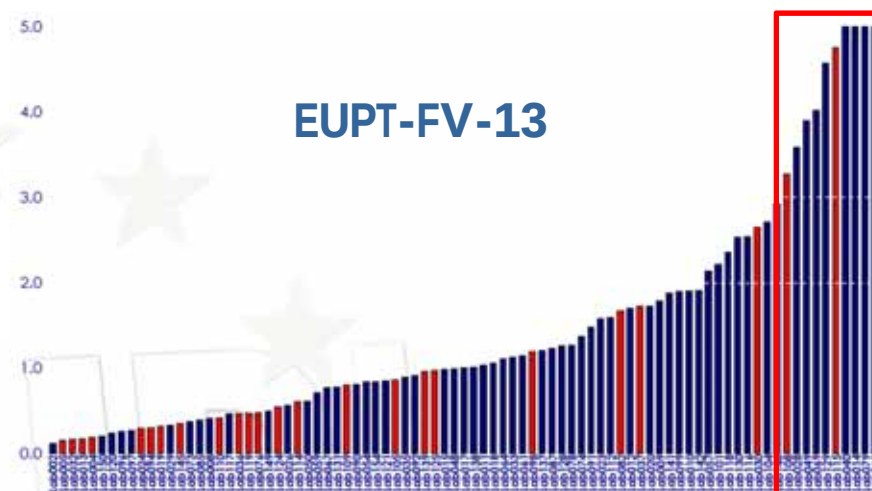
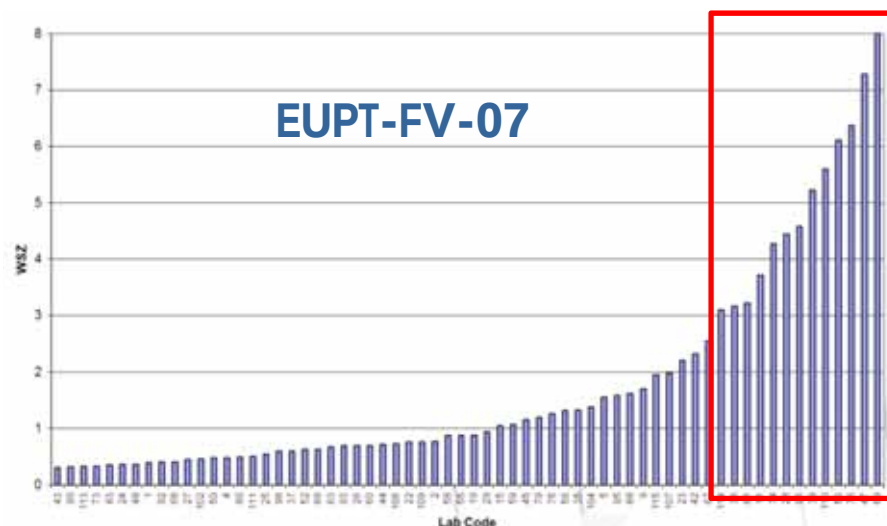
Evolution of the laboratories performance throughout the years

Labs in Category A



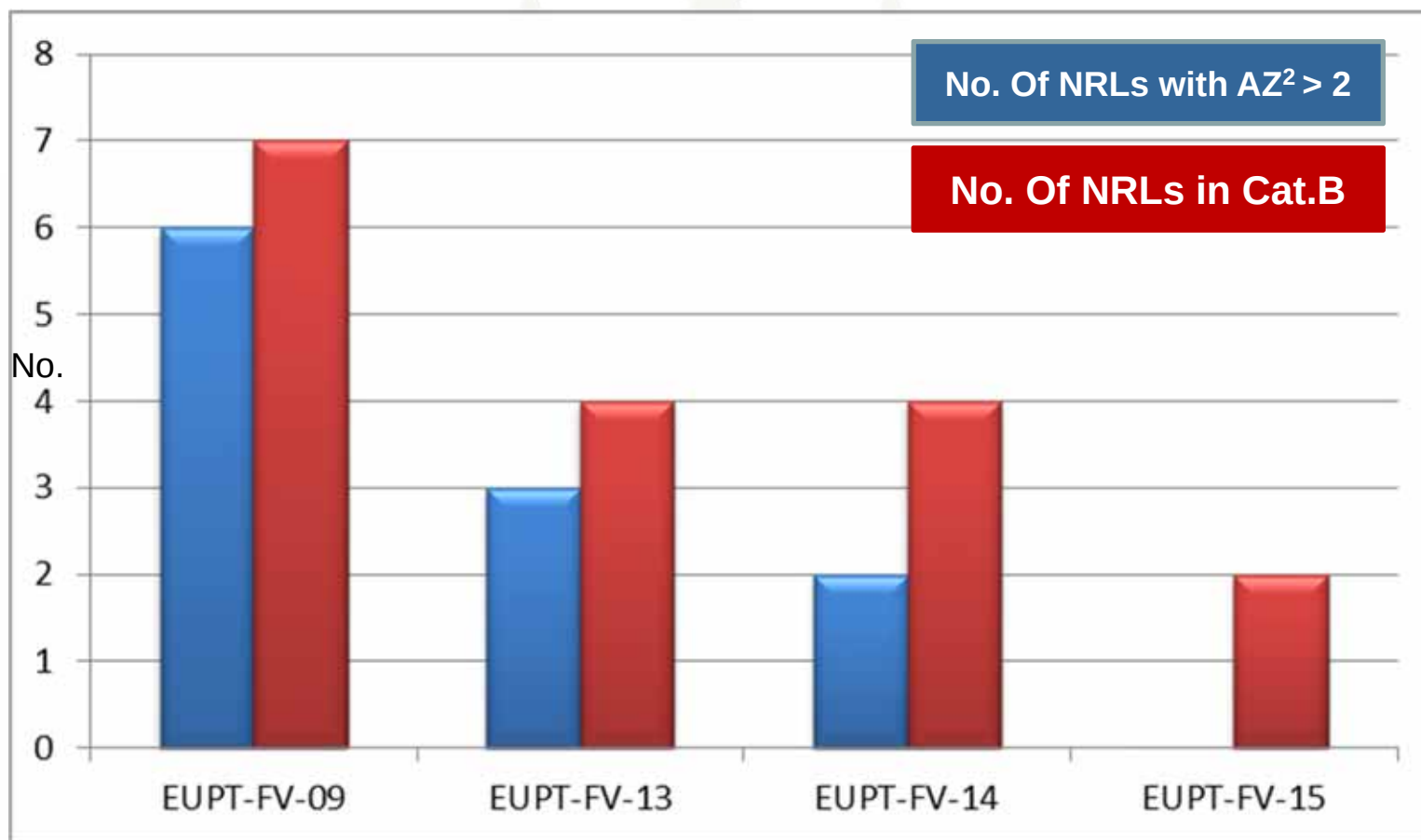
Evolution of the laboratories performance throughout the years

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

Evolution of the laboratories performance throughout the years

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

Evolution of the laboratories performance throughout the years

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.**



EURL-FV



Almería 23rd-25th October 2013

EUPT-FV-15
European Proficiency Test FV-15

Thank you for your Attention