

4th

Joint Workshop of the

EUROPEAN UNION REFERENCE LABORATORIES



Almeria
(SPAIN) 23rd-25th OCT
2013

EUROPEAN COMMISSION

PROFICIENCY TEST-T01

*PESTICIDE RESIDUES IN
TEA HOMOGENATE*



European
Commission

EURL



AMADEO R. FERNÁNDEZ-ALBA

EUROPEAN UNION REFERENCE LABORATORIES



Calendar

ACTIVITY	DATE
Sending Application Form to laboratories	9th May 2013
Sending calendar and pesticides target list to participant laboratories.	14th May 2013
Deadline for receiving Application Form from laboratories.	17th May 2013
Sample distribution.	10th June 2013
Deadline for receiving results	28th June 2013
Preliminary Report: only results, no statistical treatment.	July 2013
Final Report	October 2013



Participants

EU and EFTA countries

1	Austria
4	Belgium
1	Denmark
1	Finland
3	France
8	Germany
2	Hungary
1	Ireland
8	Italy
1	Norway*
1	Poland
1	Romania
1	Slovakia
8	Spain
1	Sweden
2	Switzerland*
2	The Netherland

*EFTA countries

Non EU and EFTA countries

1	China
1	Egypt
1	Israel
1	Saudi Arabia
1	Serbia
1	Uruguay

52 laboratories in total (16 of them NRLs)

Incurred Compounds

20 LC^a- and GC^b- amenable pesticides

15 pesticides evaluated

Acetamiprid
Buprofezin
Carbendazim
Chlorpyrifos
Cypermethrin
Difenoconazole
Endosulfan beta
Ethofenprox
Fenpropathrin
Imidacloprid
Lambda cyhalothrin
Methomyl
Parathion ethyl
Pyridaben
Tebuconazole

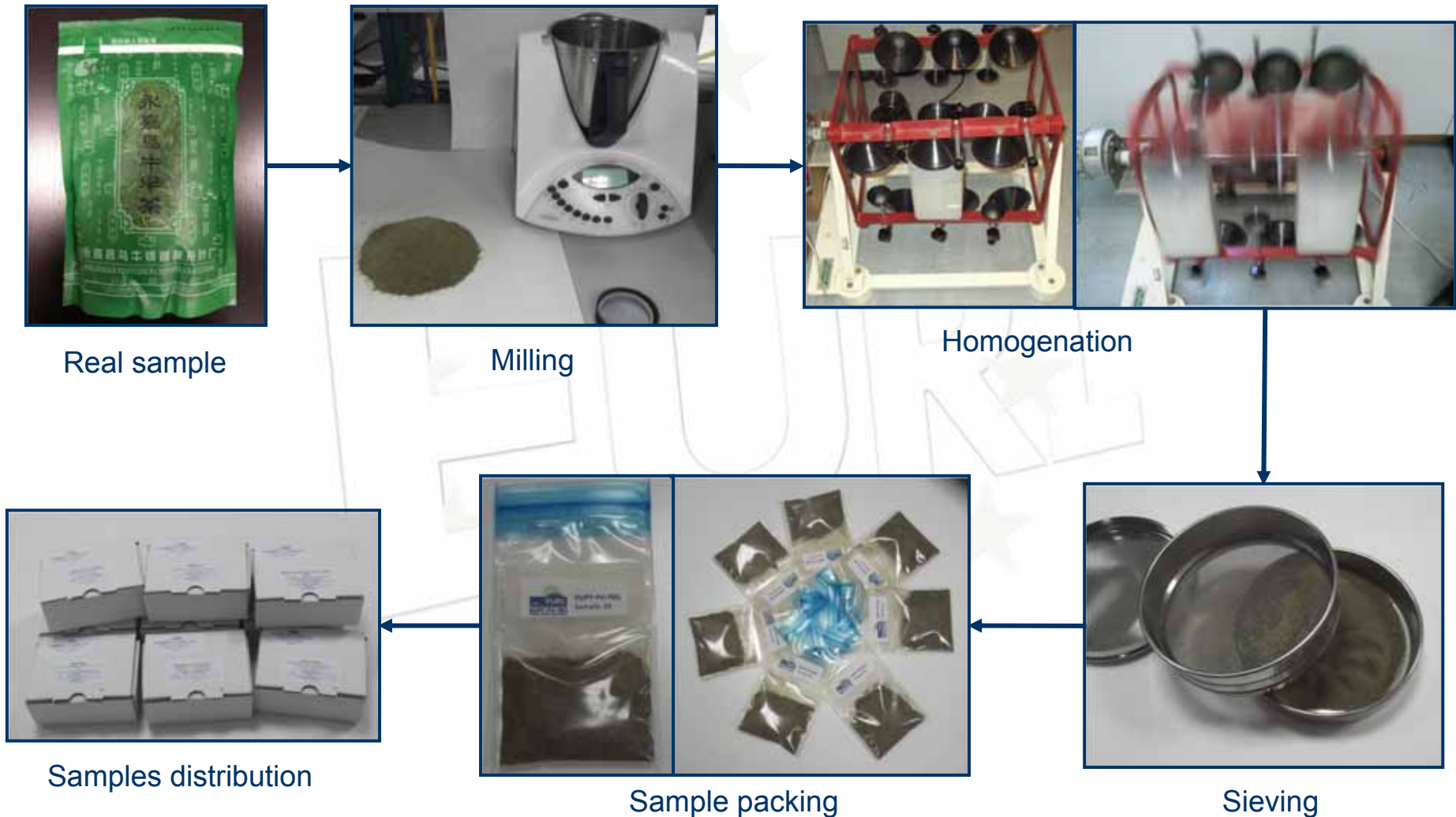
Not evaluated (Median < 4MRRL)

Bifenthrin
Endosulfan alpha
Endosulfan sulphate
Omethoate

Not evaluated (Homogeneity test fails)

Thiophanate methyl

Preparation of the test item



Homogeneity

Pesticides	Homogeneity median concentration (mg/kg)	Assigned value (mg/kg)
Acetamiprid	0.148	0.108
Buprofezin	0.213	0.180
Carbendazim	0.271	0.250
Chlorpyrifos	0.466	0.364
Cypermethrin	0.145	0.112
Difenoconazole	0.380	0.367
Endosulfan beta	0.096	0.081
Ethofenprox	0.234	0.170
Fenpropathrin	0.258	0.188
Imidacloprid	0.108	0.081
Lambda cyhalothrin	0.175	0.141
Methomyl	0.113	0.089
Parathion ethyl	0.436	0.372
Pyridaben	0.338	0.268
Tebuconazole	0.423	0.338
Thiophanate methyl*	0.259	0.190

*Homogeneity test fails



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Results

Summary of reported results

Pesticides	No. of Reported Results	No. of False Negative Results	No. of Not Analysed Results	Percentage of Reported Results (out of 46)*
Acetamiprid	36	4	6	78
Bifenthrin*	19	22	5	41
Buprofezin	41	3	2	89
Carbendazim	42	0	4	91
Chlorpyrifos	43	1	2	93
Cypermethrin	31	6	9	67
Difenoconazole	40	1	5	87
Endosulfan alpha*	36	5	5	78
Endosulfan beta	38	3	5	83
Endosulfan sulfate*	39	2	5	85
Ethofenprox	36	2	8	78
Fenpropathrin	40	1	5	87
Imidacloprid	33	7	6	72
Lambda cyhalothrin	44	0	2	96
Methomyl	29	9	8	63
Omethoate*	20	19	7	43
Parathion ethyl	40	2	4	87
Pyridaben	44	1	1	96
Tebuconazole	42	1	3	91
Thiophanate methyl**	35	2	9	76

*Median < 4 MRRL

**Homogeneity test fails

False positives

Laboratory Code	Pesticide	Concentration (mg/kg)	Determination Technique	RL (mg/Kg)	MRRL (mg/Kg)	Extraction method used
Lab007	Orthophenylphenol	0.020	LC-MS/MS (QQQ)	0.01	0.02	QuEChERS
Lab009	Penconazole	0.071	LC-MS/MS (QQQ)	0.01	0.02	Modified QuEChERS with CaCl ₂
Lab011	Amitraz	0.126	LC-MS/MS (QQQ)	0.02	0.02	Modified QuEChERS with CaCl ₂
Lab012	Methidathion	0.041	GC-MS/MS (QQQ)	0.01	0.02	L-L extraction
Lab013	Carbaryl	0.042	Other	0.02	0.02	Modified QuEChERS with CaCl ₂
Lab034	Folpet	0.056	GC-MS/MS (QQQ), FPD, ECD	0.02	0.02	miniLuke
Lab035	Ethoprophos	0.155	LC and GC MS/MS (QQQ)	0.01	0.02	QuEChERS
Lab043	Ethoprophos	0.177	LC-MS/MS (QQQ)	0.01	0.02	QuEChERS
Lab043	Triazophos	0.196	LC-MS/MS (QQQ)	0.01	0.02	QuEChERS

False negatives

Laboratory Code	Acetamiprid	Buprofezin	Chlorpyrifos	Cypermethrin (cypermethrin incl. other mixtures of constituent isomers (sum of isomers))	Difenoconazole	Endosulfan beta	Etofenprox	Fenpropathrin	Imidacloprid	Methomyl	Parathion-ethyl	Pyridaben	Tebuconazole	Thiophanate-methyl
Lab003									ND	ND				
Lab006	ND													
Lab007				ND						ND				ND
Lab010		ND												
Lab011									ND	ND				
Lab013			ND											
Lab016				ND		ND			ND	ND				
Lab018				ND										
Lab020									ND					
Lab022											ND	ND	ND	
Lab025				ND						ND				
Lab026										ND				
Lab027	ND								ND	ND	ND			
Lab033		ND												
Lab034		ND						ND						
Lab035							ND							
Lab039				ND										
Lab043				ND		ND	ND							
Lab047						ND								
Lab050														ND
Lab051	ND								ND	ND				
Lab054	ND				ND				ND	ND				

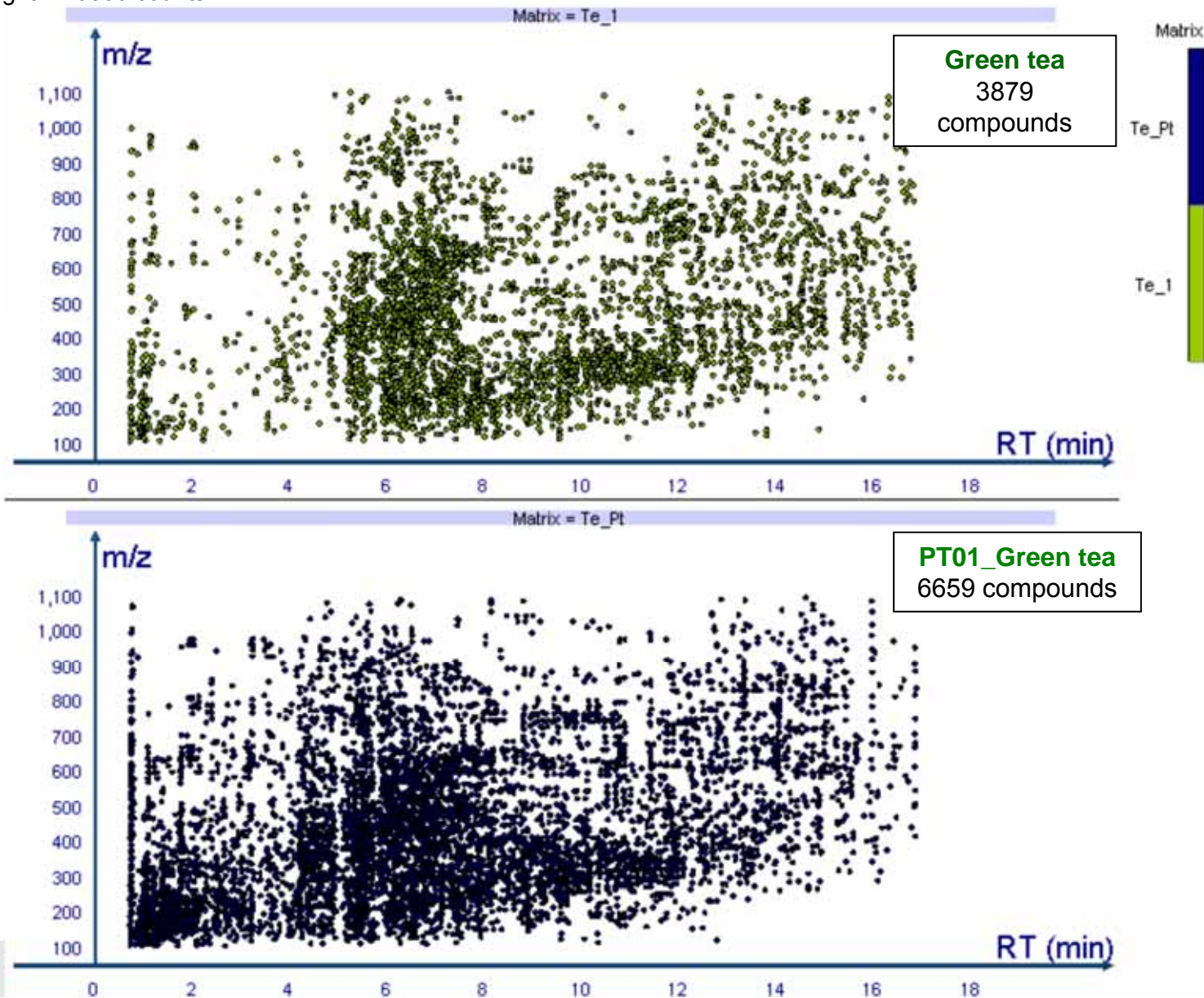
- QuEChERS
- CaCl₂
- EtAc
- MiniLuke
- MeOH
- Other

False negatives (%) over the total number of results per extraction method

QuEChERS: 6.9%
 CaCl₂: 6.3%
 Ethyl Acetate method: 2.3%
 MeOH extraction: 6.7%
 miniLuke: 6.1%
 Other methods: 2.2%



Tea matrix compounds. QuEChERS_CaCl₂ extraction method. Dilution:5 LC-TOF-MS
Absolute height ≥ 10000 counts



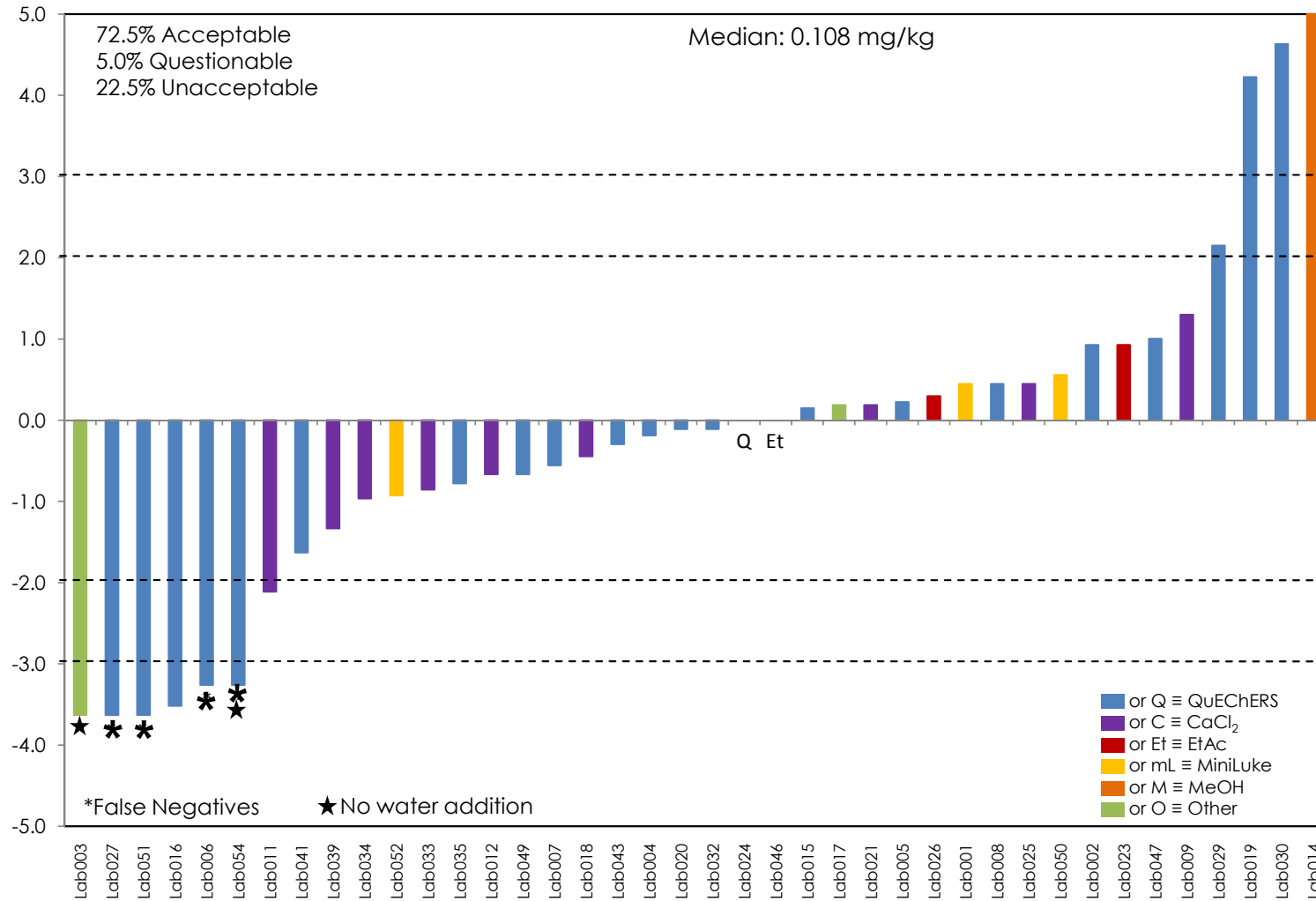
Median values, uncertainty and %RSDs for all pesticides present in the test item

Pesticides	MRRL (mg/Kg)	Median (mg/Kg)	u (mg/kg)	FFP RSD (%)	Qn RSD (%)
Acetamiprid	0.02	0.108	0.007	25	31
Buprofezin	0.02	0.180	0.014	25	39
Carbendazim	0.02	0.250	0.021	25	44
Chlorpyrifos	0.02	0.364	0.021	25	35
Cypermethrin	0.02	0.112	0.011	25	44
Difenoconazole	0.02	0.367	0.018	25	25
Endosulfan beta	0.02	0.081	0.007	25	44
Ethofenprox	0.01	0.170	0.012	25	34
Fenpropathrin	0.02	0.188	0.008	25	22
Imidacloprid	0.02	0.081	0.006	25	36
Lambda cyhalothrin	0.02	0.141	0.009	25	33
Methomyl	0.02	0.089	0.007	25	32
Parathion ethyl	0.02	0.372	0.021	25	29
Pyridaben	0.02	0.268	0.017	25	32
Tebuconazole	0.02	0.338	0.017	25	26



Z-Scores

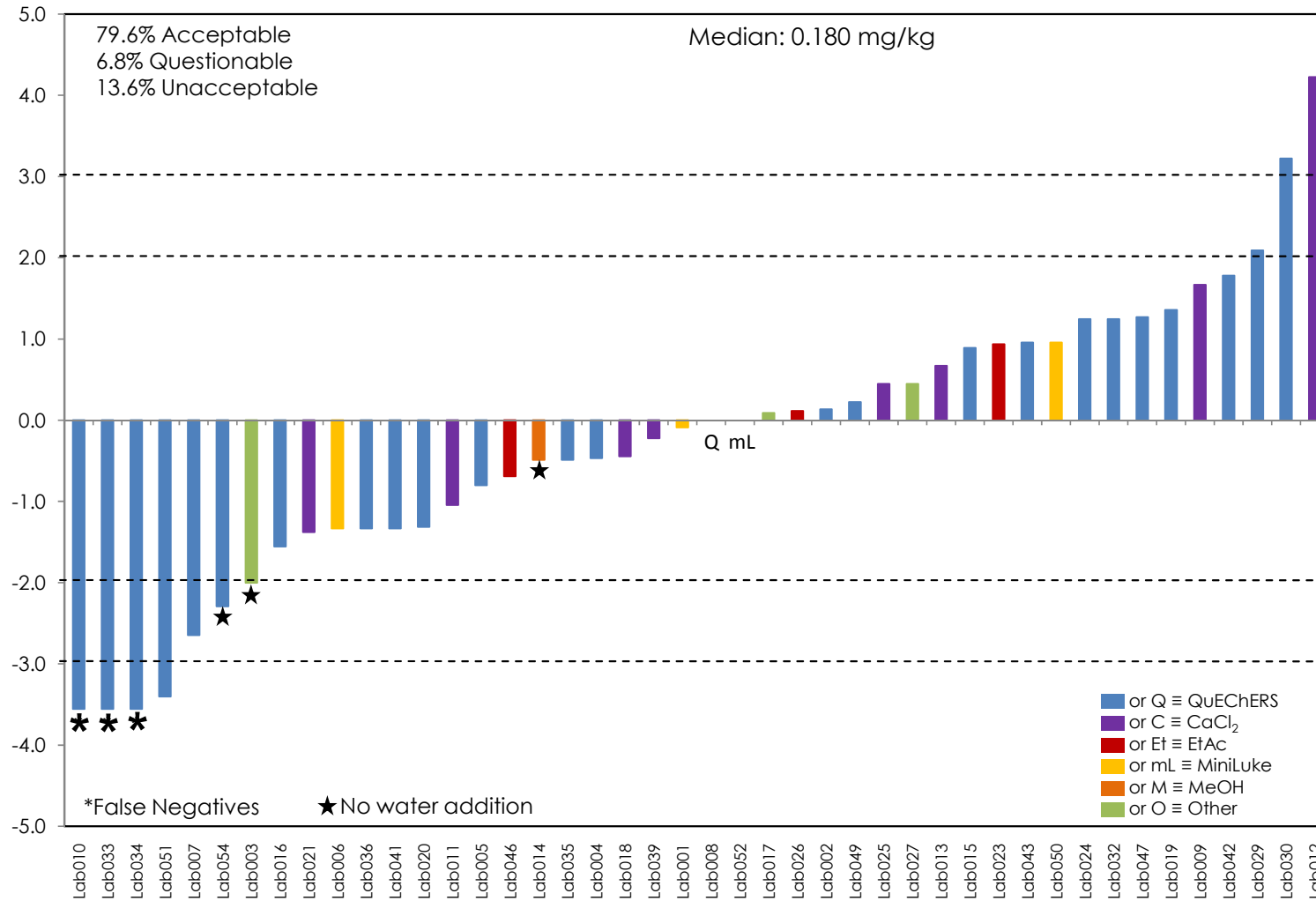
Acetamiprid





Z-Scores

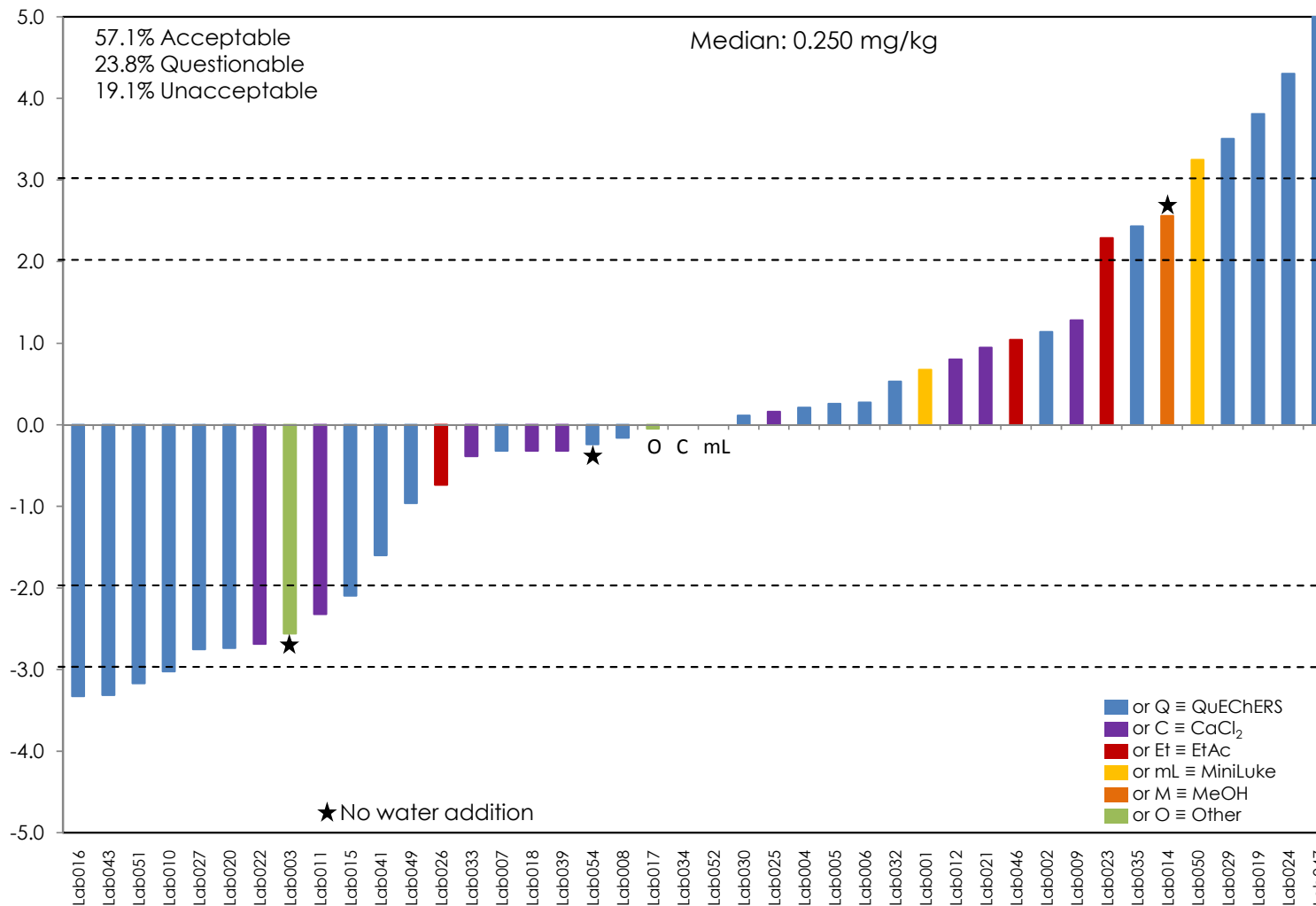
Buprofezin





Z-Scores

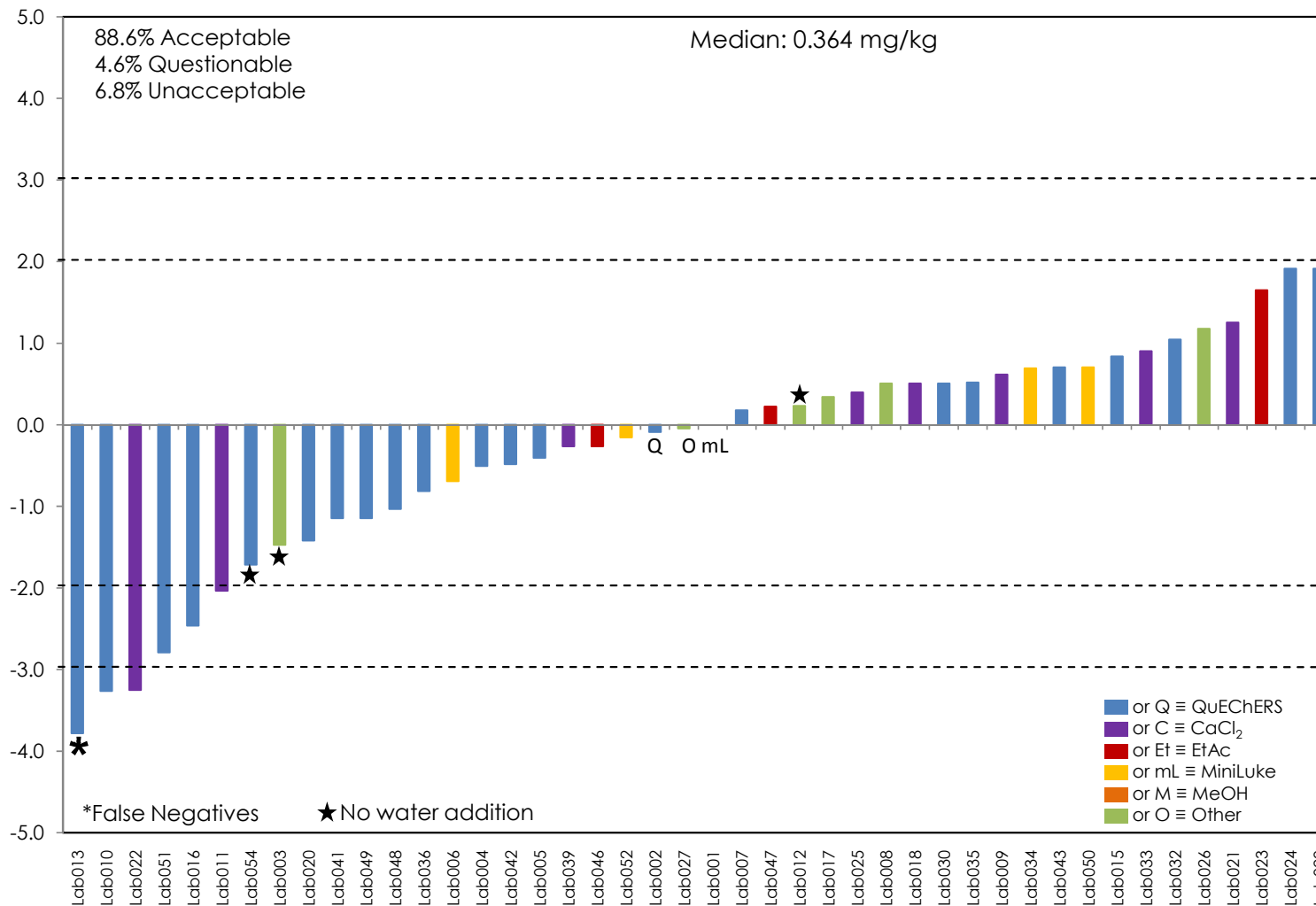
Carbendazim





Z-Scores

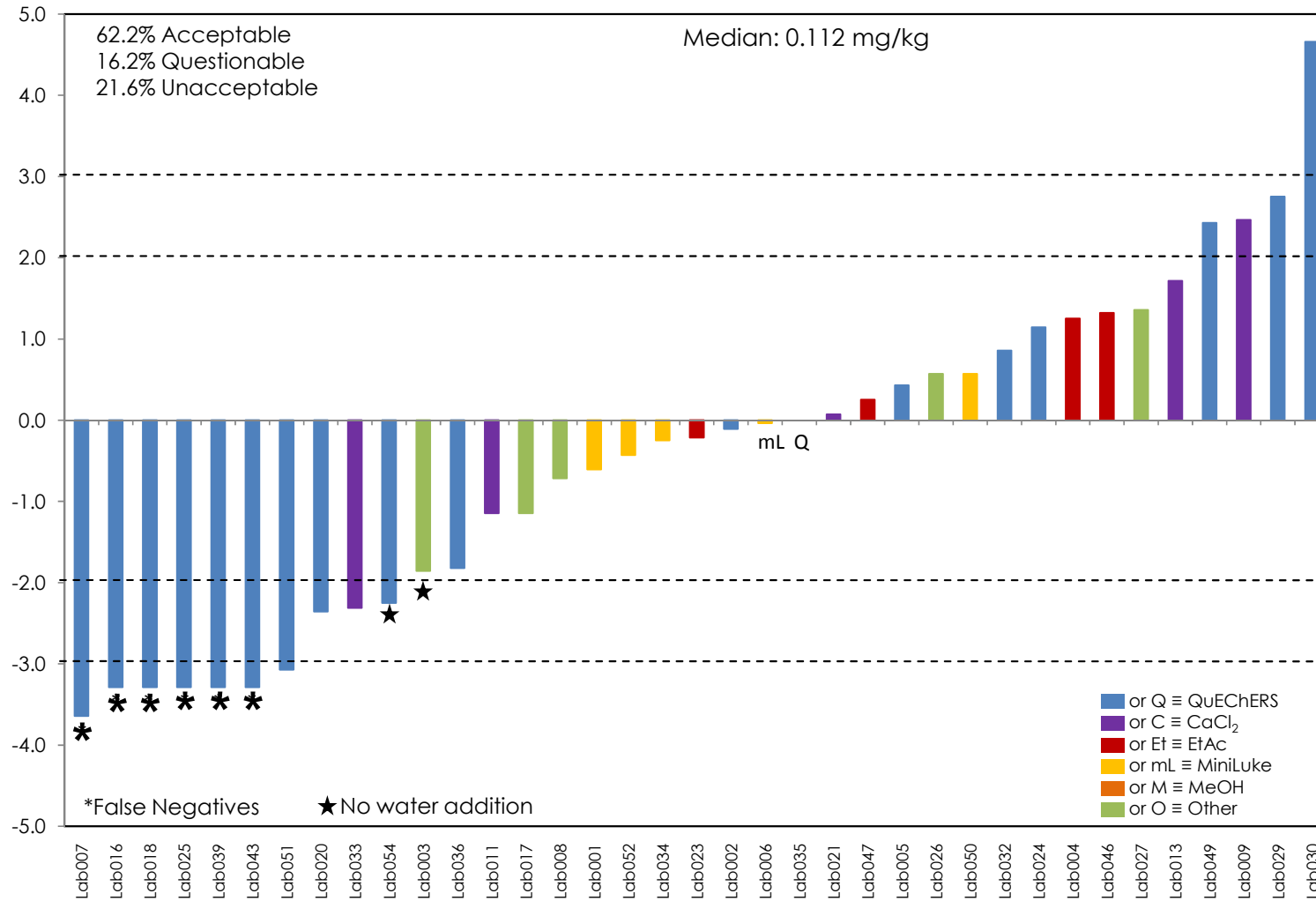
Chlorpyrifos





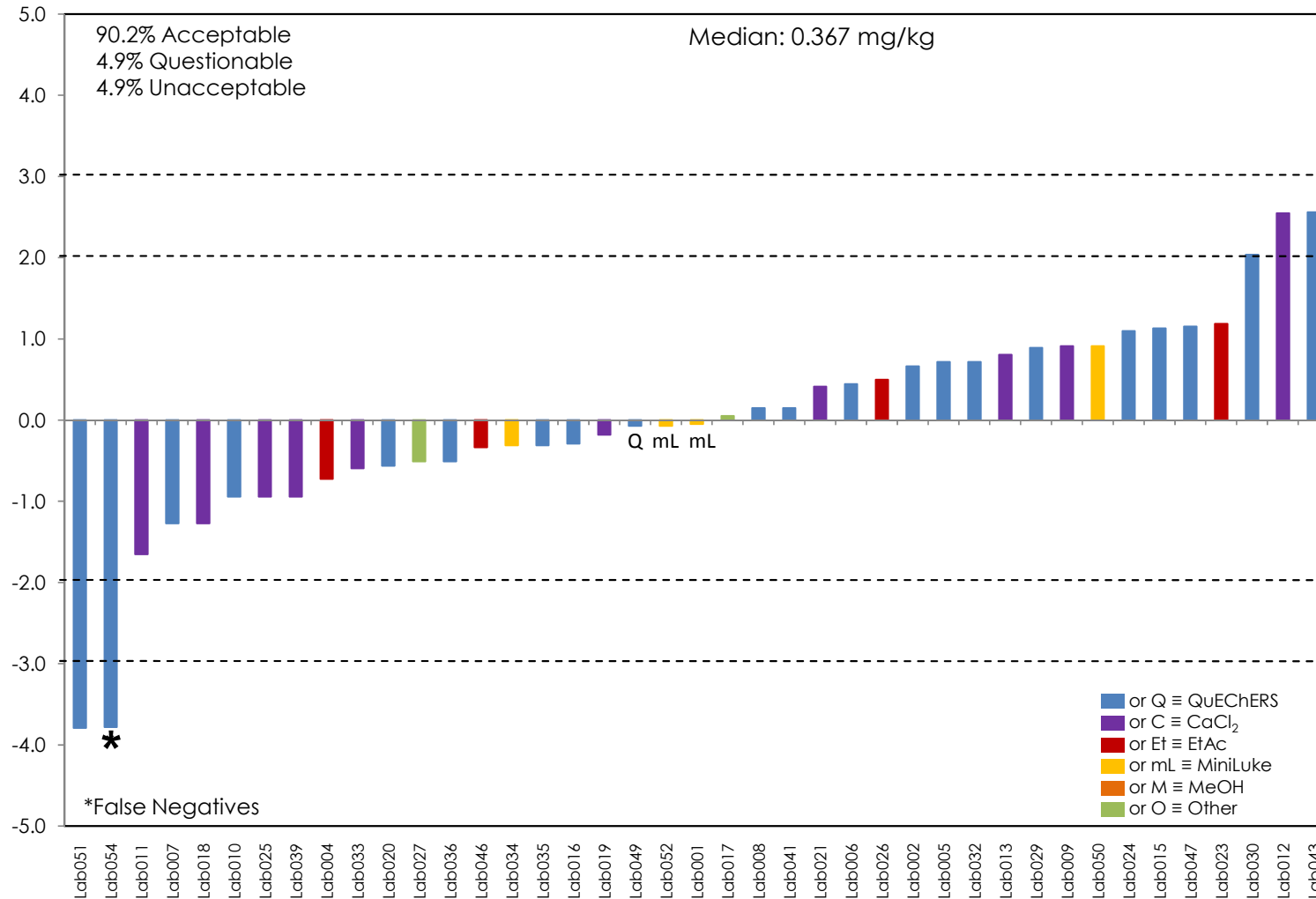
Z-Scores

Cypermethrin



Z-Scores

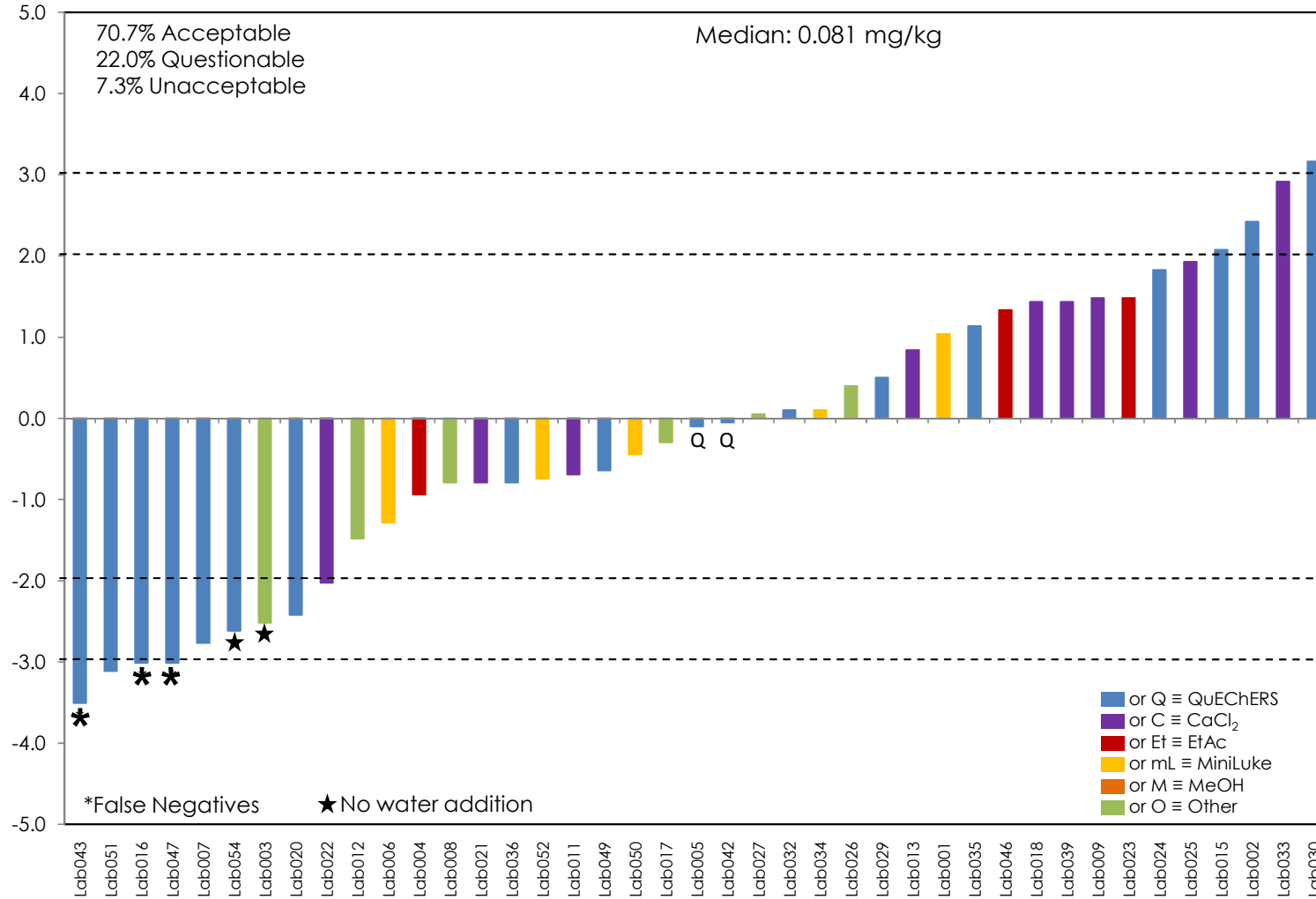
Difenoconazole





Z-Scores

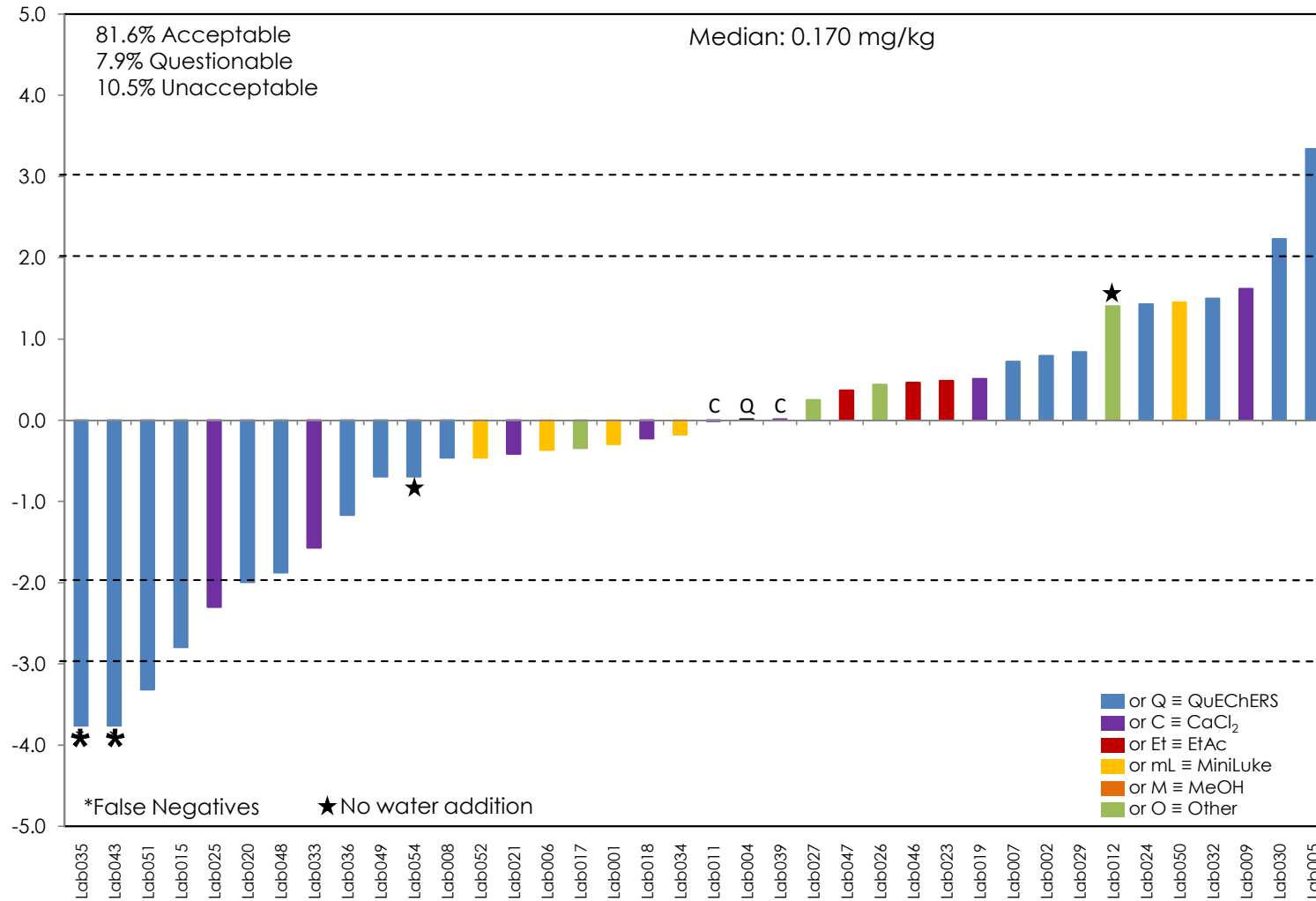
Endosulfan beta





Z-Scores

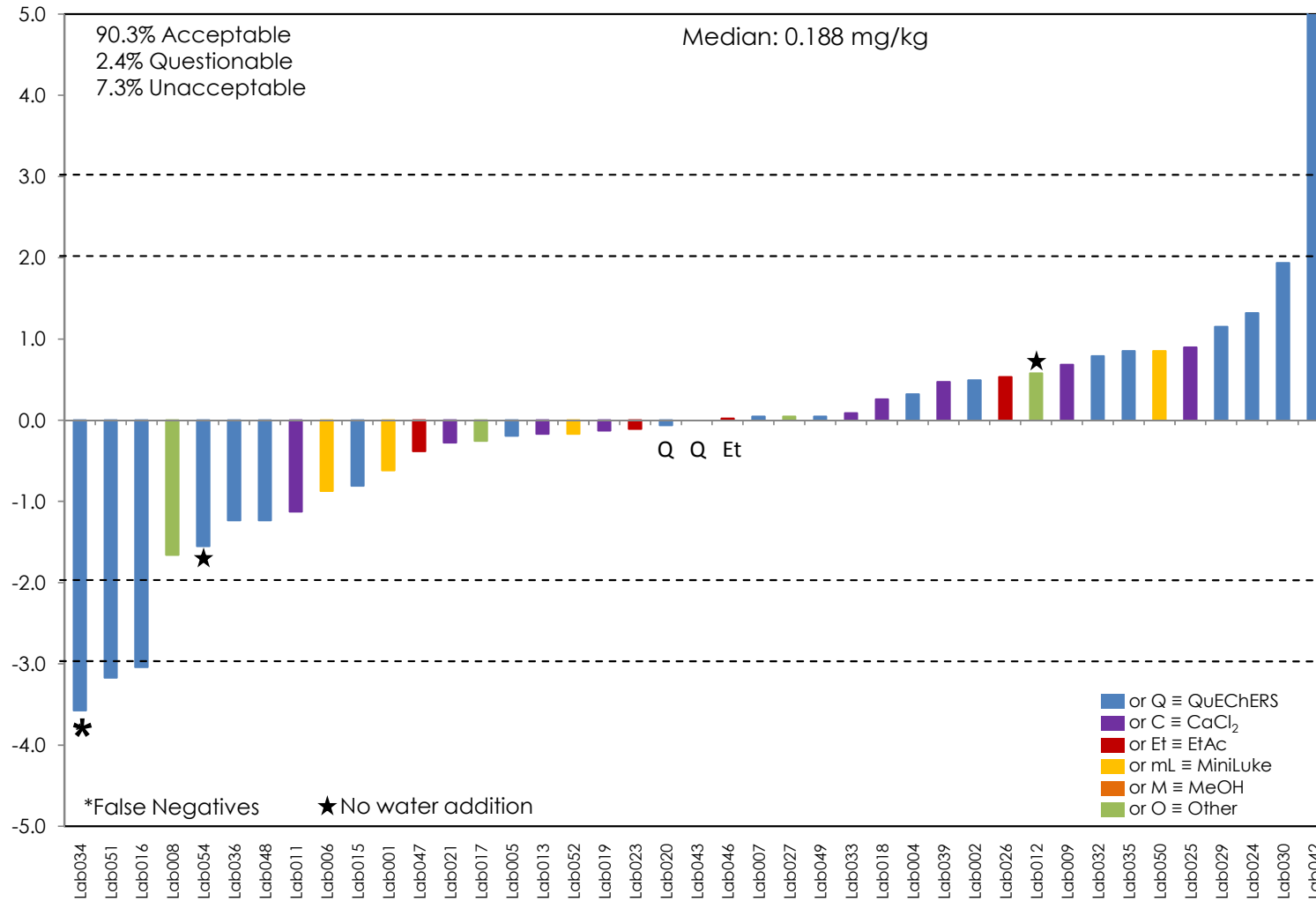
Etofenprox





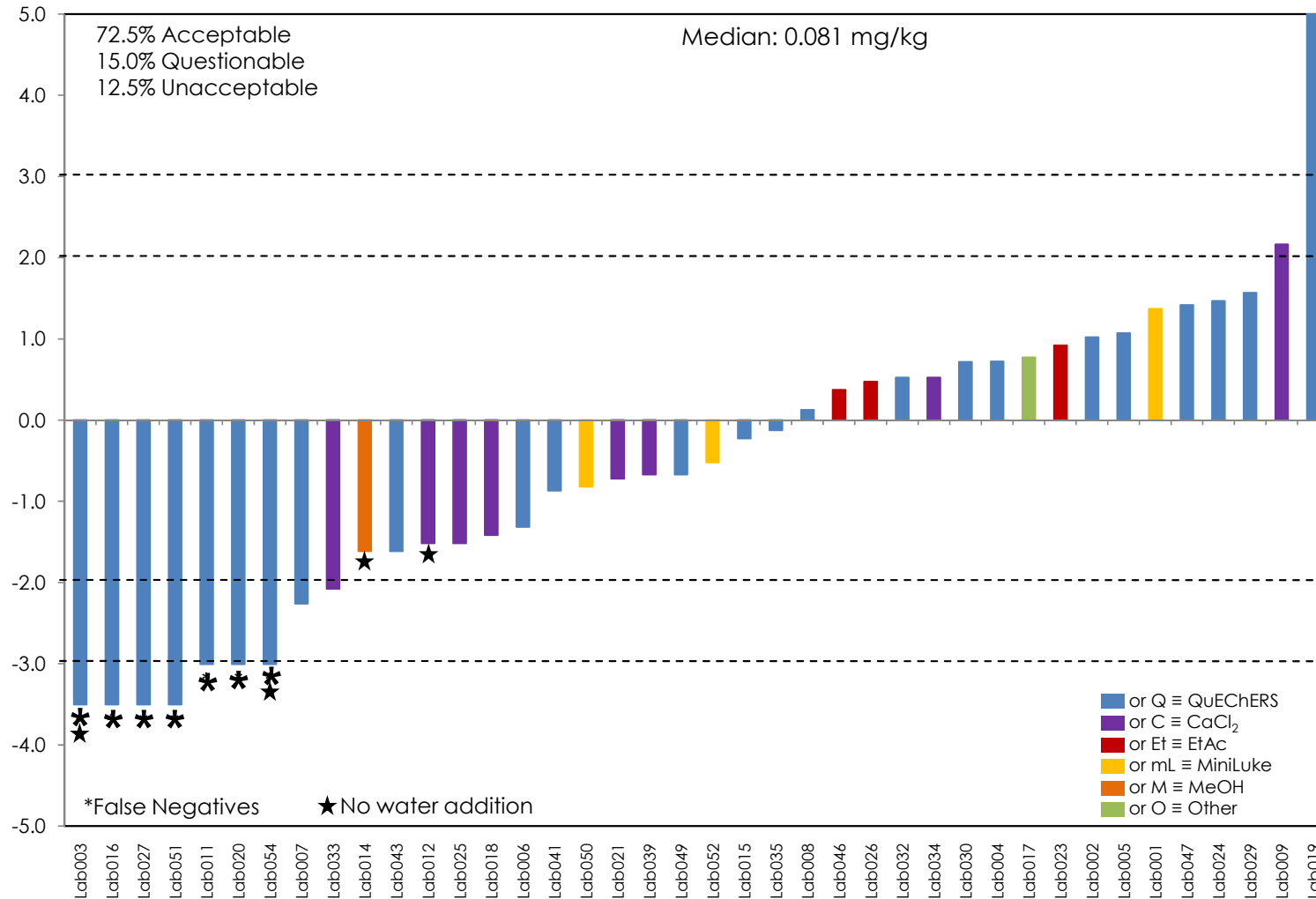
Z-Scores

Fenpropathrin



Z-Scores

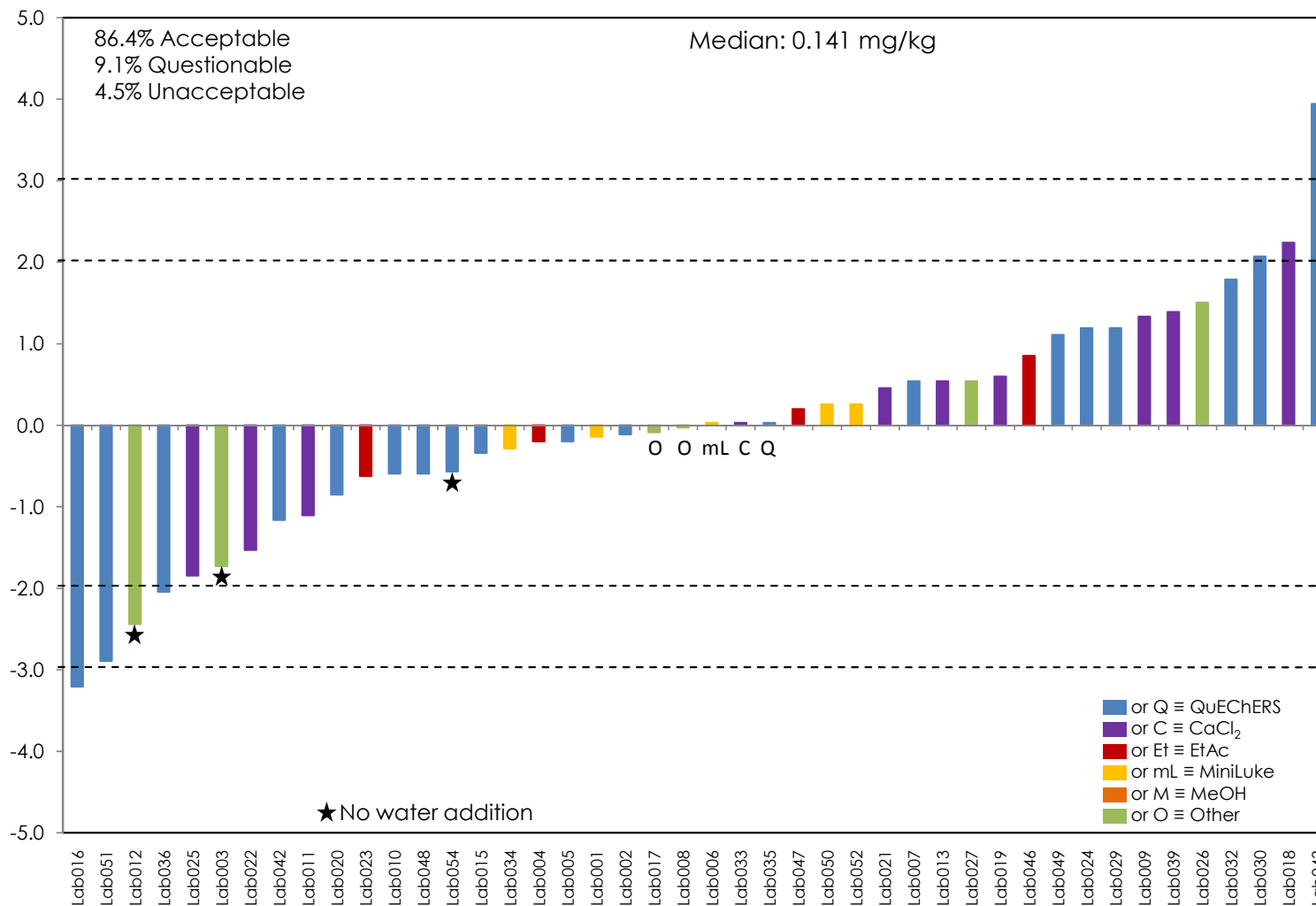
Imidacloprid





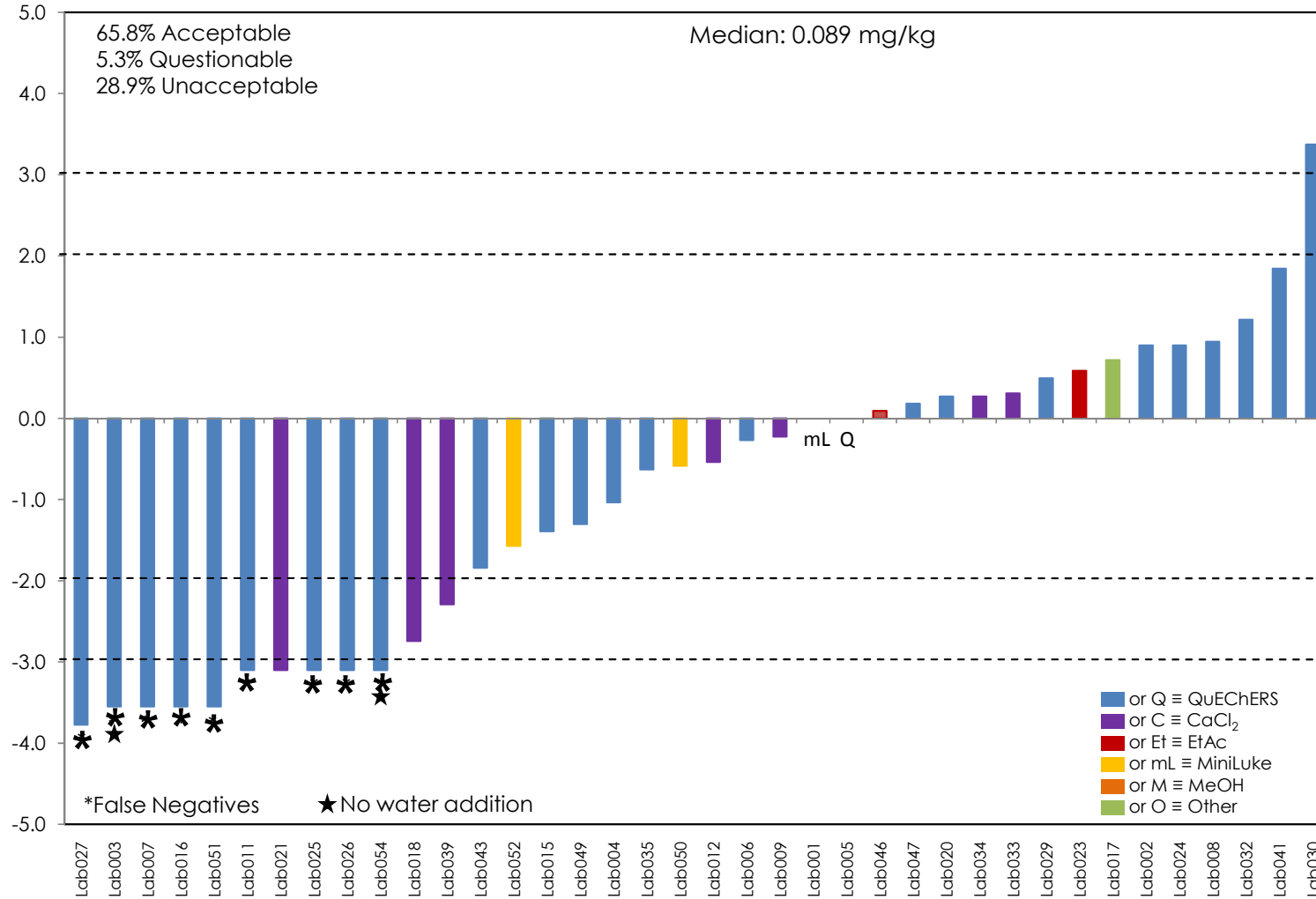
Z-Scores

Lambda cyhalothrin



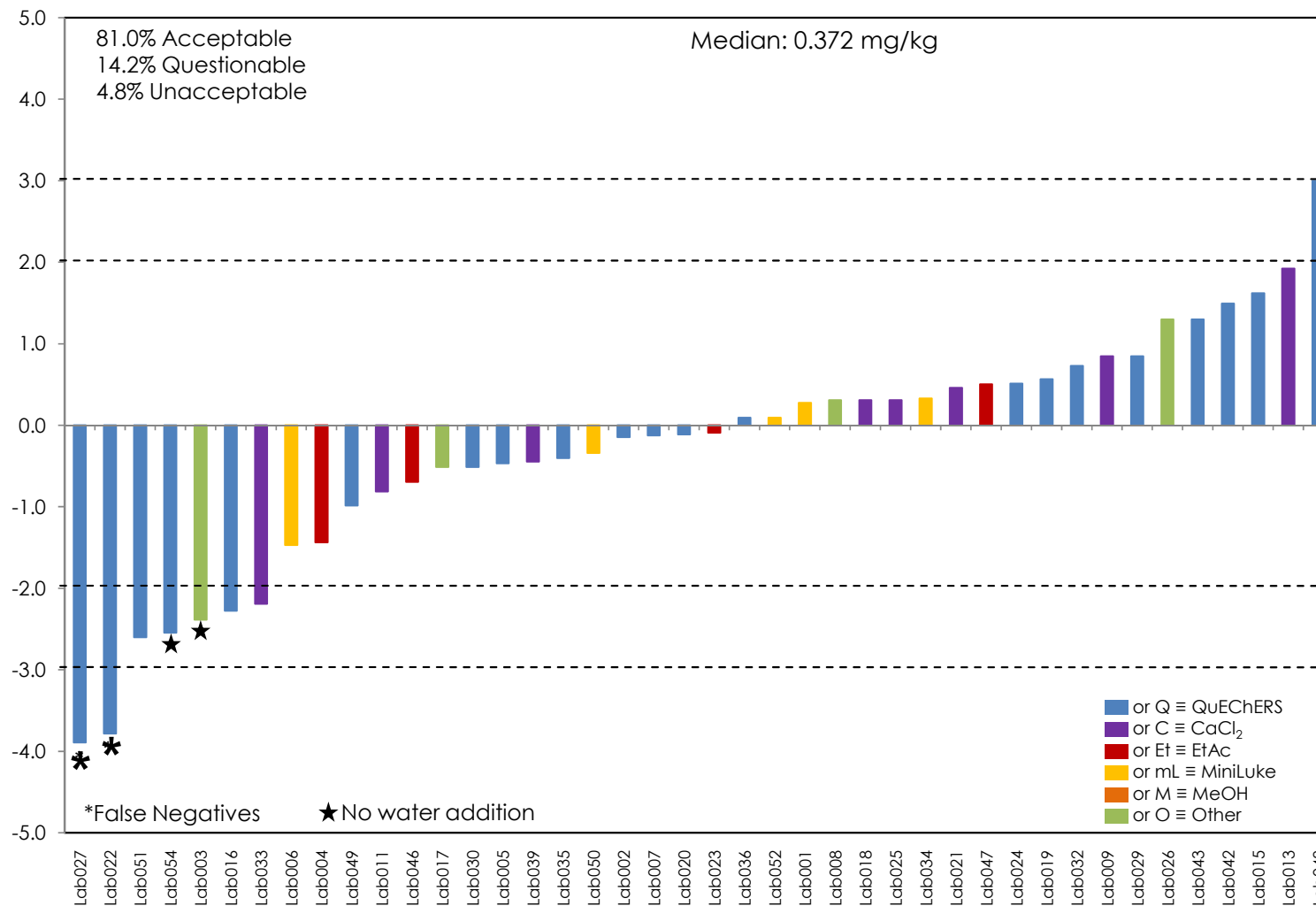
Z-Scores

Methomyl



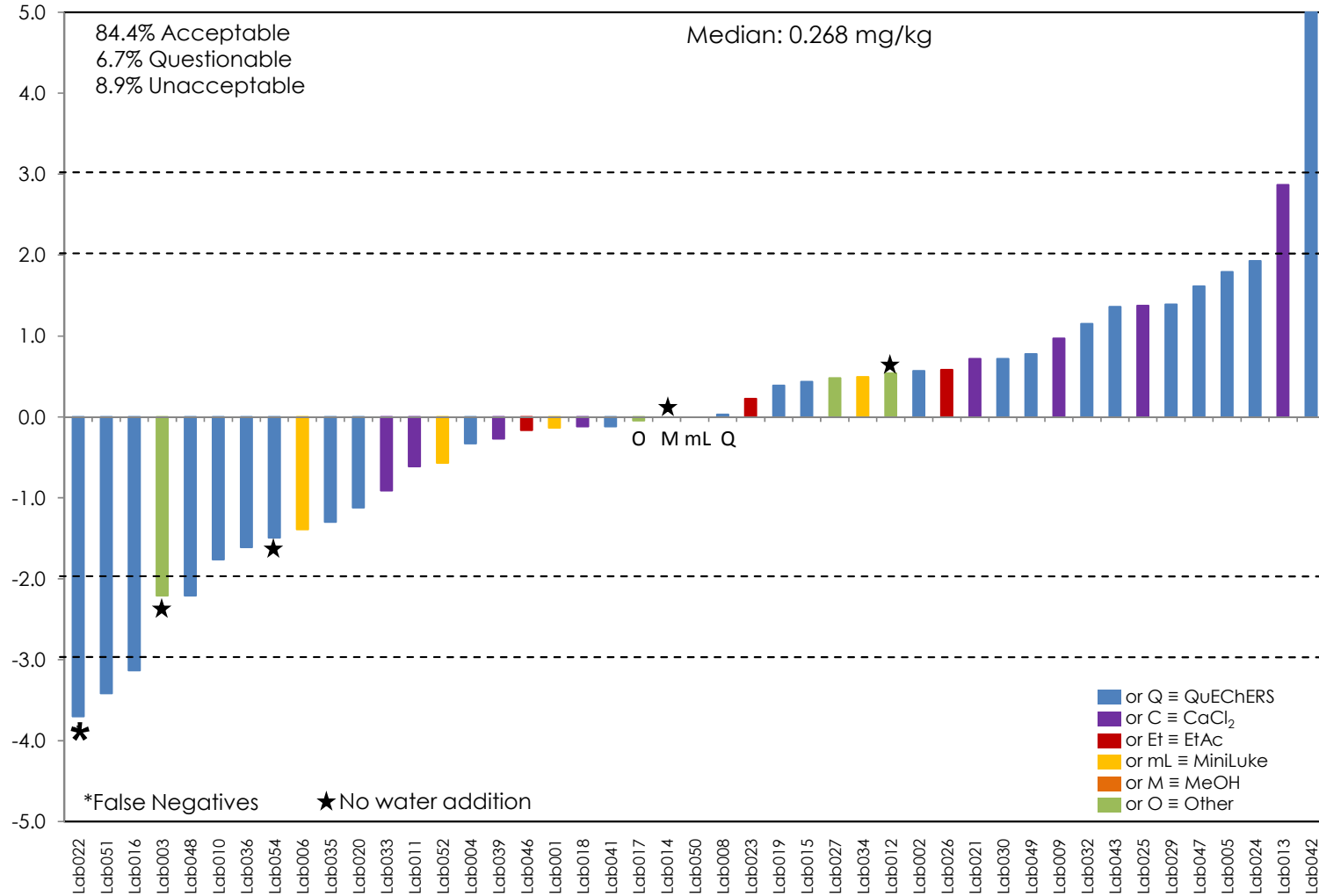
Z-Scores

Parathion-ethyl



Z-Scores

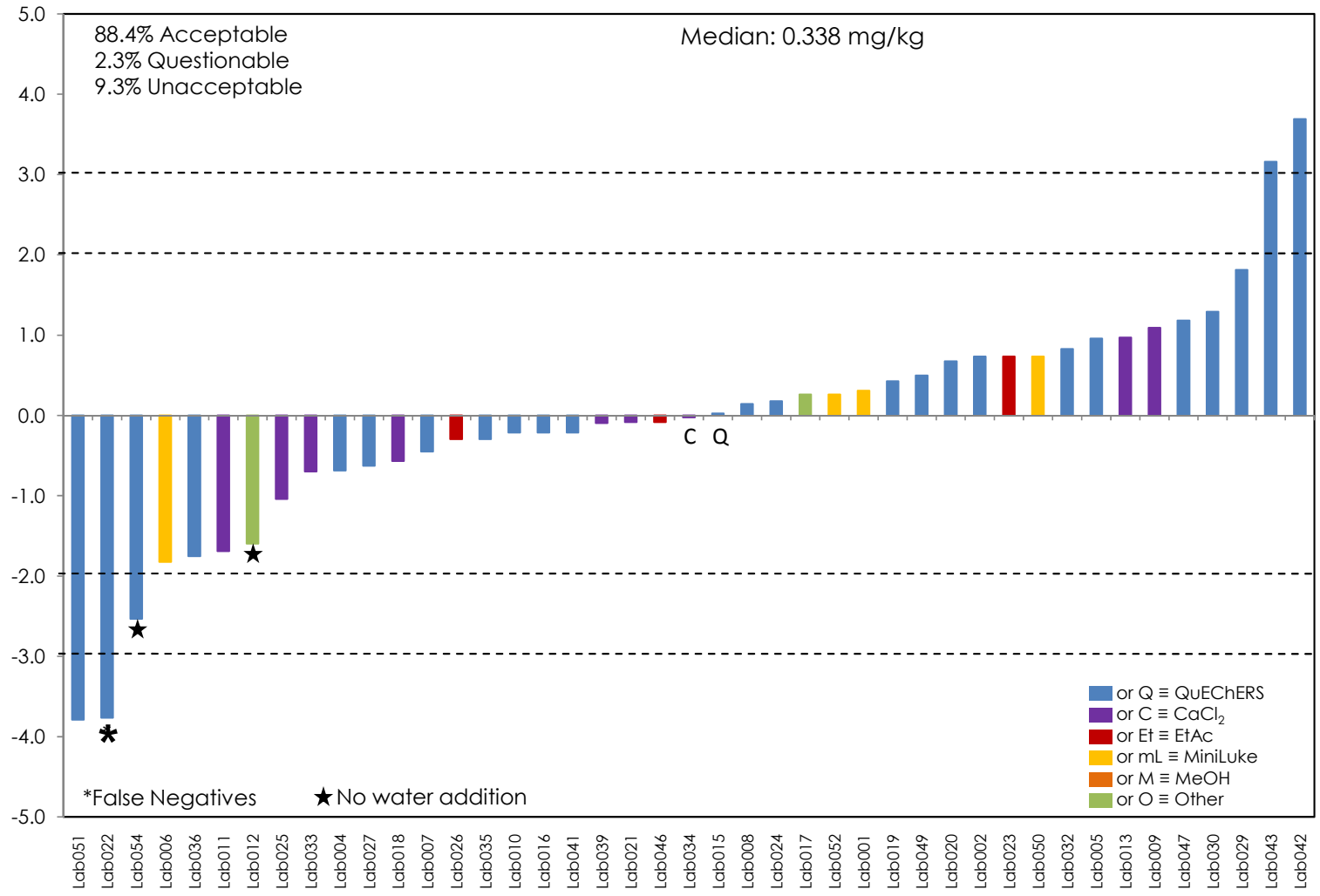
Pyridaben





Z-Scores

Tebuconazole

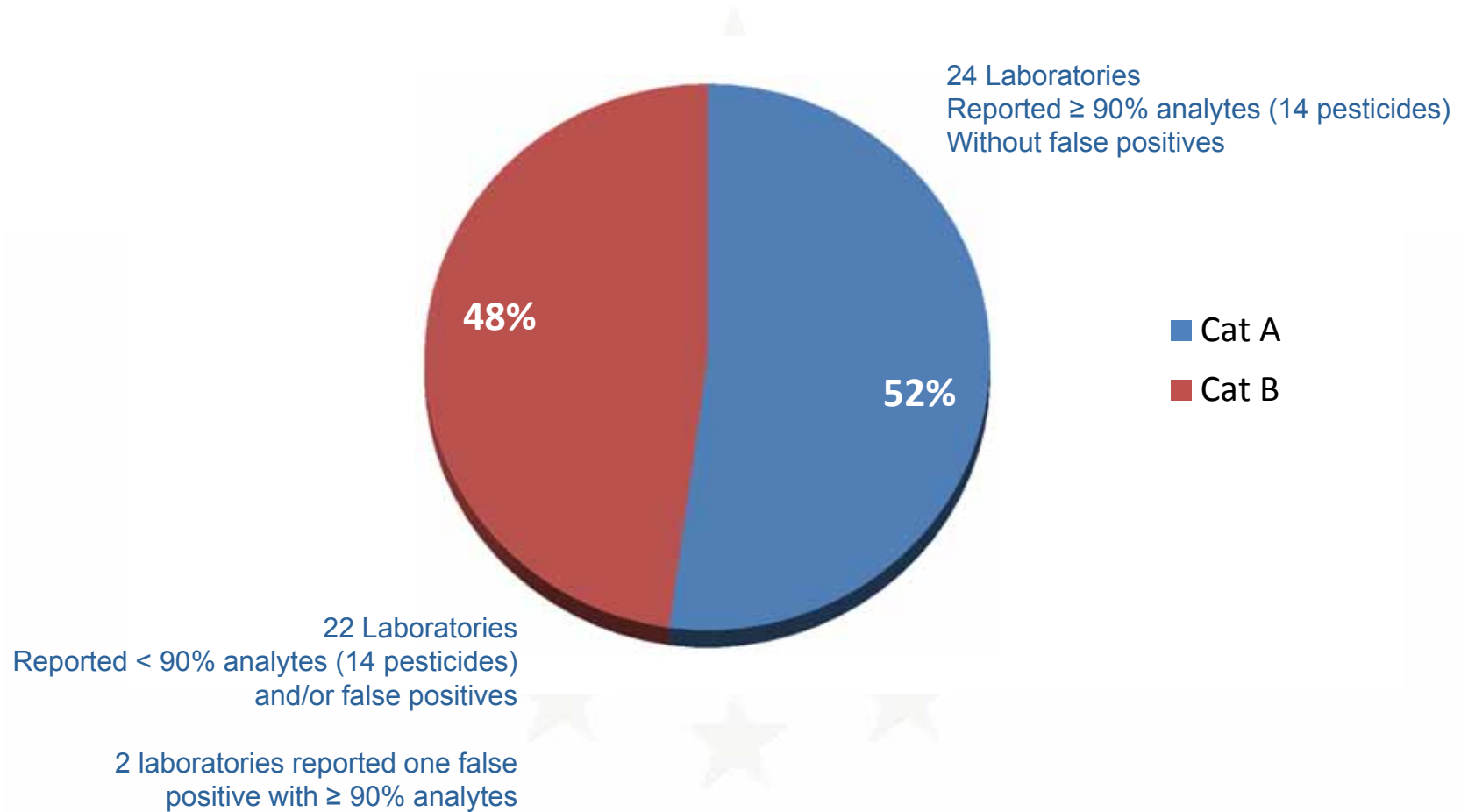


Classification of Z-scores for the pesticides reported

Pesticides	Acceptable (%)	Questionable (%)	Unacceptable (%)
Acetamiprid	72.5	5.0	22.5
Buprofezin	79.6	6.8	13.6
Carbendazim	57.1	23.8	19.1
Chlorpyrifos	88.6	4.6	6.8
Cypermethrin	62.2	16.2	21.6
Difenoconazole	90.2	4.9	4.9
Endosulfan beta	70.7	22.0	7.3
Ethofenprox	81.6	7.9	10.5
Fenpropathrin	90.3	2.4	7.3
Imidacloprid	72.5	15.0	12.5
Lambda cyhalothrin	86.4	9.1	4.5
Methomyl	65.8	5.3	28.9
Parathion ethyl	81.0	14.2	4.8
Pyridaben	84.4	6.7	8.9
Tebuconazole	88.4	2.3	9.3



Category A and B





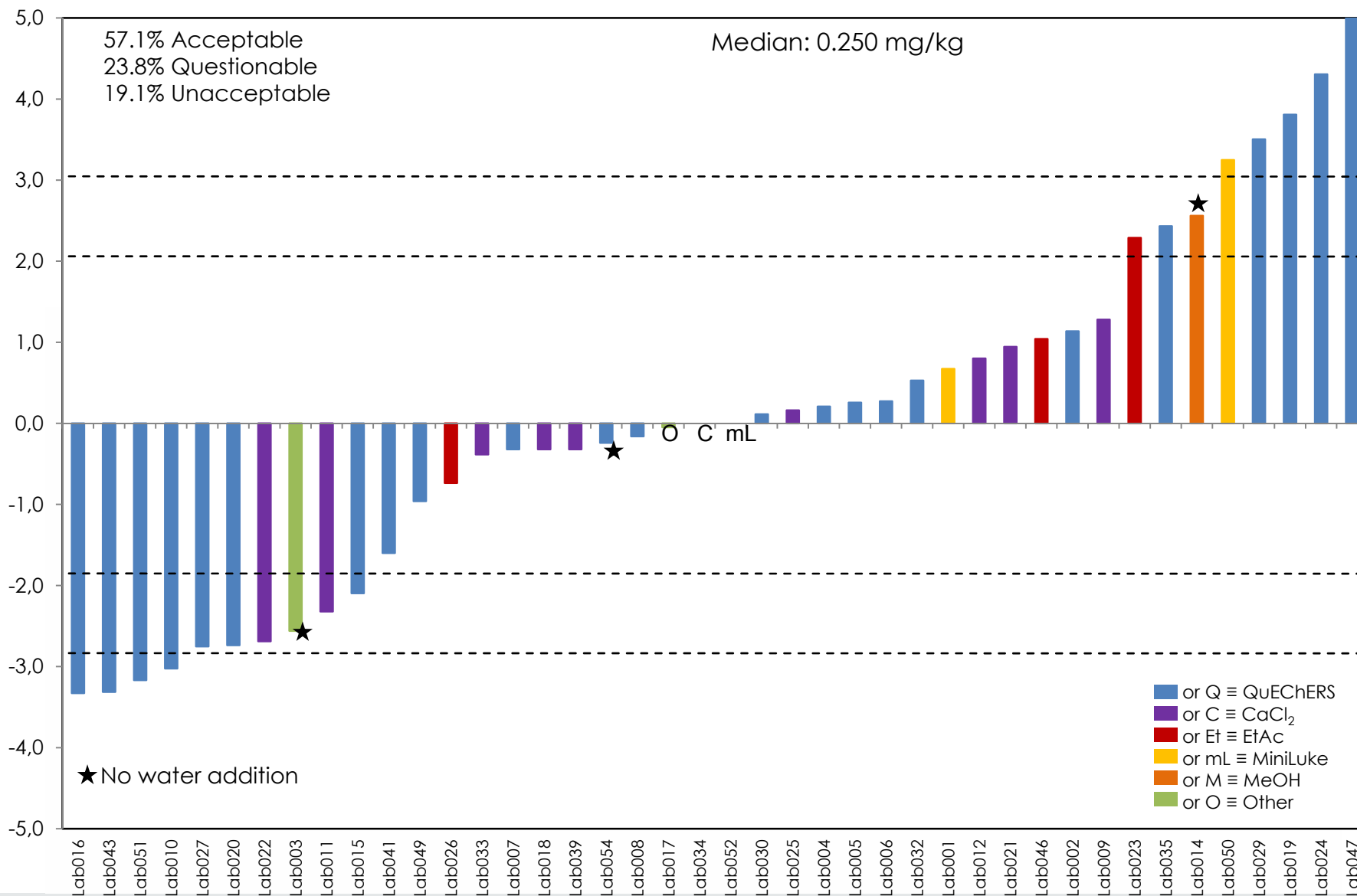
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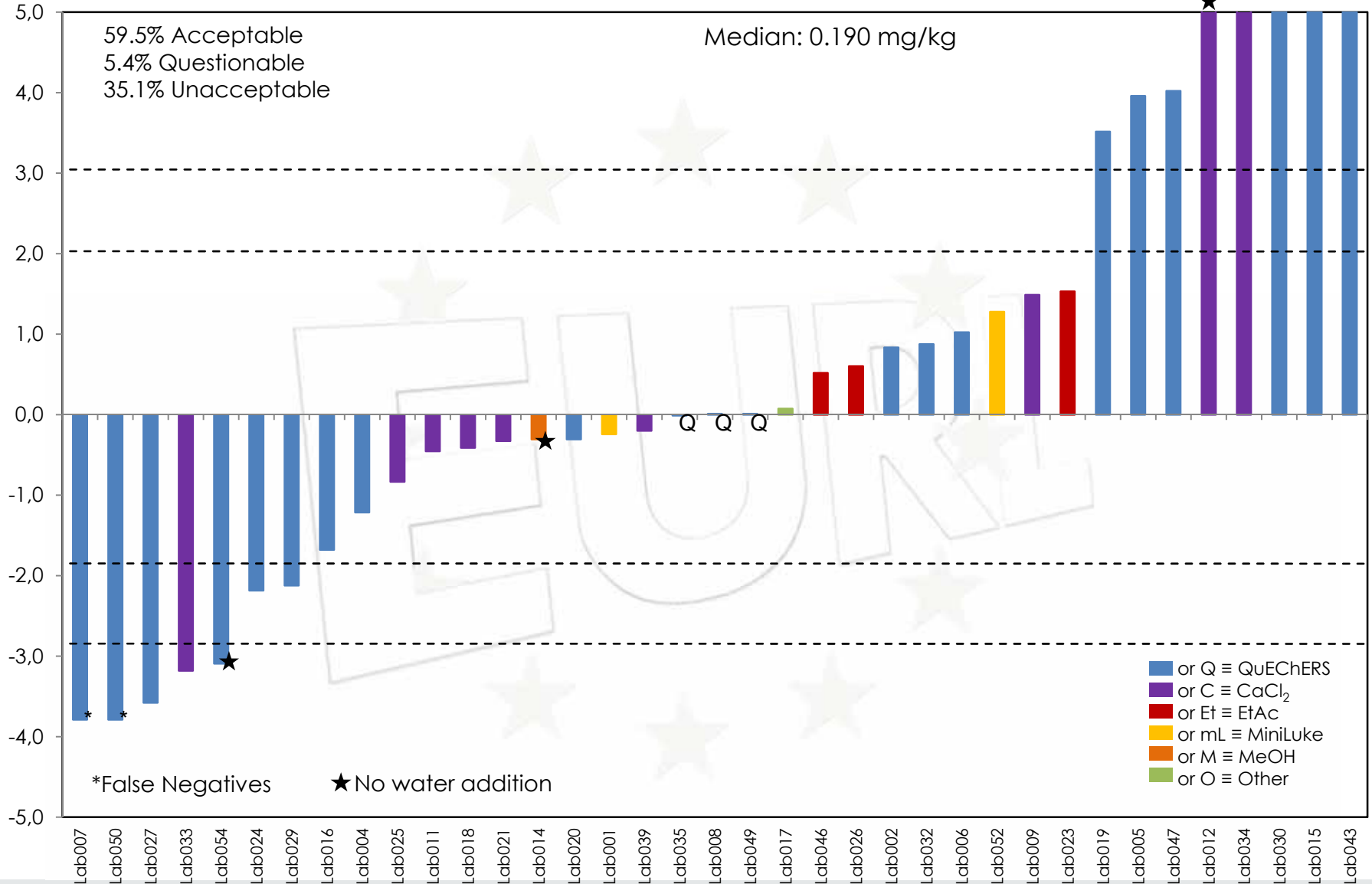
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Special case

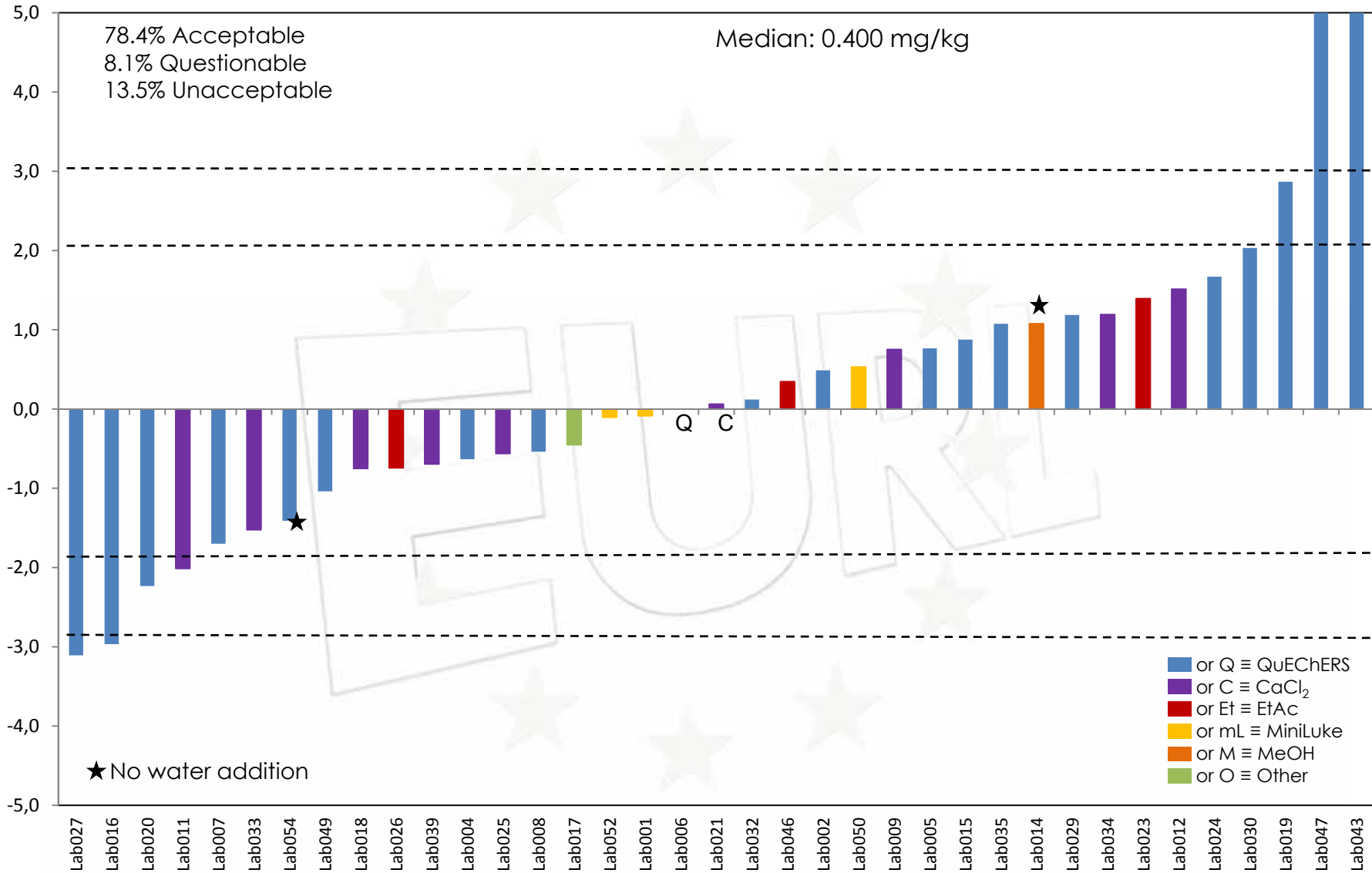
Carbendazim



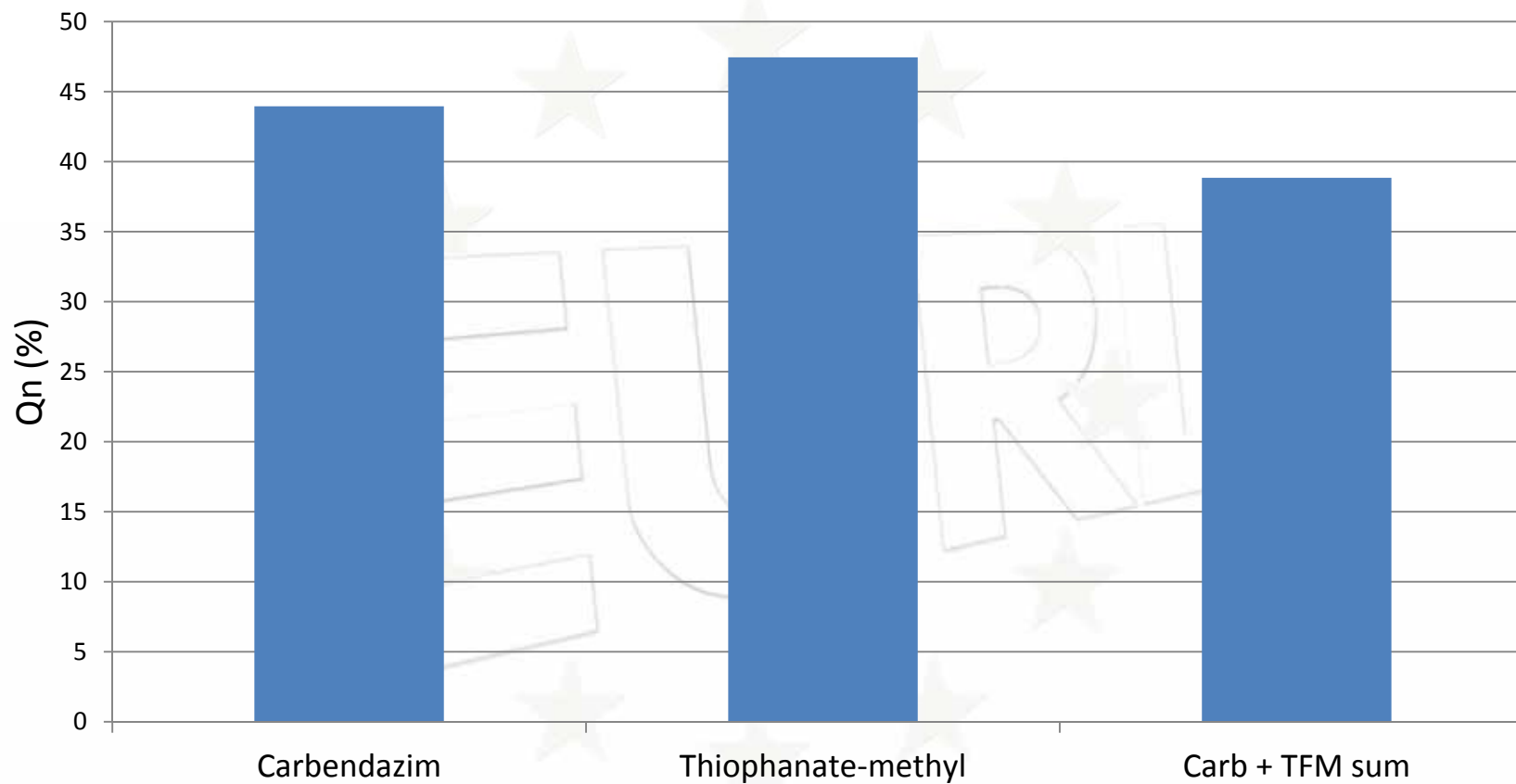
Thiophanate methyl



Carbendazim + Thiophanate methyl expressed as Carbendazim

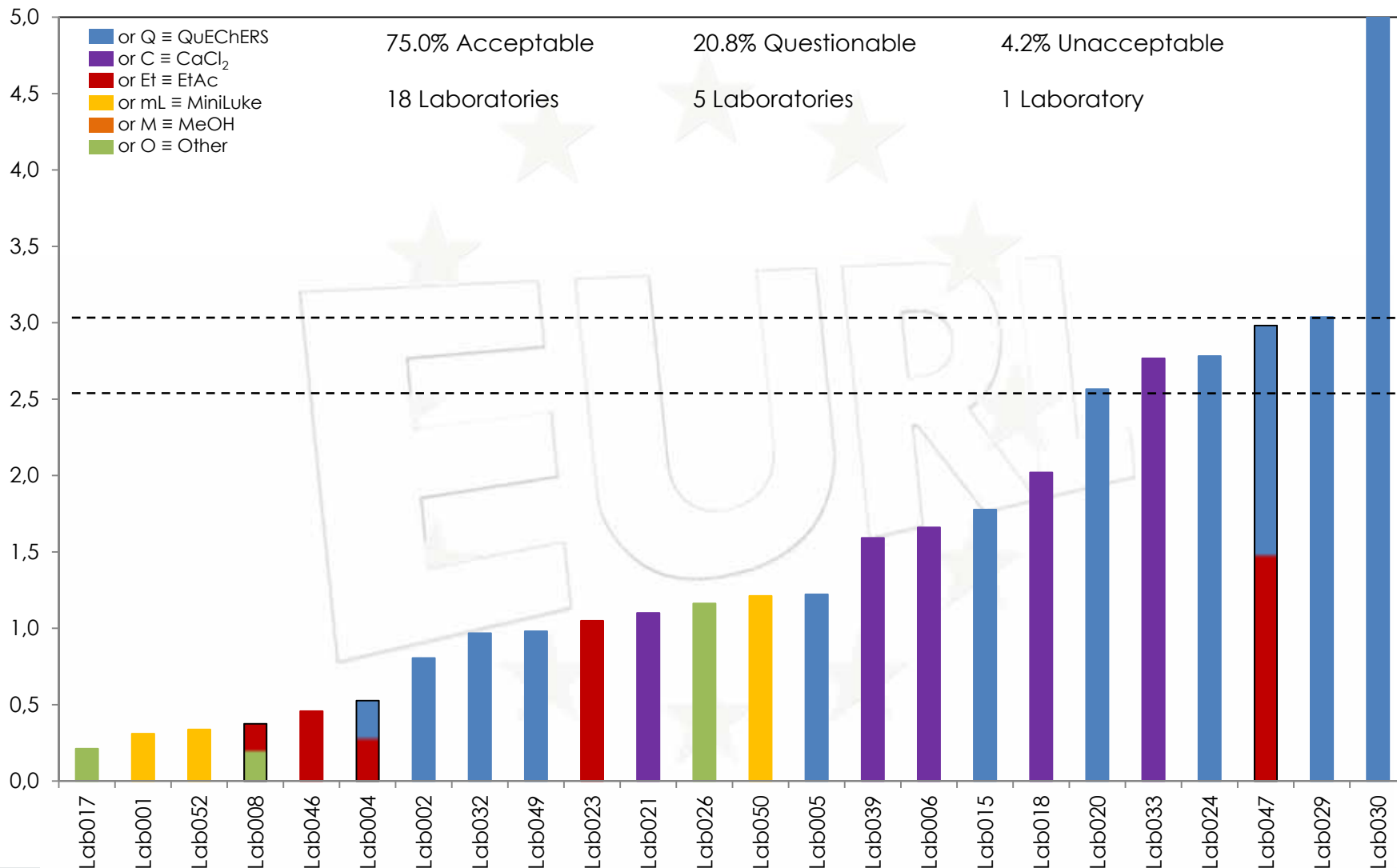


Qn (%)



Graph using individual values for Carbendazim and Thiophanate methyl

EUPT-PT01 Graphical representation for laboratories in Category A





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Conclusions

Conclusions

- Fifty-two laboratories participated in EUPT-T01 (Six from non EU or EFTA countries, 16 NRLs).
- Pesticides considered as positives were those which were reported by both the Organiser and the majority of participants.
- A higher dispersion (Qn) than in most fruits and vegetables have been observed (As maximum 44%).
- For carbendazim and thiophanate methyl, the results were influenced by the different degrees of degradation obtained by participants during the sample handling.
- QuEChERS without calcium chloride addition modification, presented a higher dispersion accounted as Qn than for the whole data reported (average Qn for QuEChERS was 41% whereas for the combined data, it was 34%).
- One compound did not pass the homogeneity test (thiophanate methyl). This fact is clearly as a consequence of some degradation to carbendazim.
- Overall, the results can be considered to be good with regard to the z-scores for each pesticide present in the test item, except for some pesticides which obtained a value more than 20% of unacceptable results (3 of them).
- It would appear that multiresidue methods such as QuEChERS have improved following modification (CaCl₂ addition).
- All of the laboratories applying the miniLuke method obtained acceptable results in terms of z-scores, except for carbendazim.