National Food Institute

Technical University of Denmark

DTU

EU proficiency test on Cereals – CRL for Cereals and Feedingstuff EU-PTC2 (part 1)

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Copenhagen, 18 September 2008

CRL Community Reference Laboratory – Pesticides in Cereals and Feedingstuff – National Food Institute DTU – DG SANCO EUROPEAN COMMISSION

Calendar

Activity	Dates
Sample Treatment, milling, homogenisation and storage. Homogeneity and stability tests.	September 2007- January 2008
Invitation to laboratories to participate, including Calendar, Pesticide List, instructions on how to register, and link to website for further information e.g. Protocol and how to report results and methods used	November 2007
Deadline for receiving Application Form from invited laboratories.	20 January 2008
Test material distribution.	18 February 2008
Deadline for receipt of results on the online submission website	16 March 2008
Preliminary Report	May 2008
Final Report	October 2008

Participation

Austria *	4	Latvia *	1
Belgium *	3	Lithuania *	1
Bulgaria *	1	Luxembourg *	1
Cyprus *	1	Norway	1
Czech Republic **	3	Poland **	7
Denmark *	2	Portugal *	3
Estonia *	1	Romania **	2
Finland *	1	Slovakia *	1
France *	2	Slovenia **	3
Germany *	9	Spain **	4
Greece **	3	Sweden *	2
Hungary *	2	The Netherlands **	2
Ireland *	1	UK *	1
Italy *	10	Total 27 countries	72

Participation NRLs

- 74 laboratories registered representing 27 countries and 26 Member States
- 72 laboratories submitted results
- 33 of these were NRL representing 26 Member state
- Assosiates – Norway

PT-C2 Possible pesticide list

*Alpha-cypermethrin
*Azoxystrobin
*Bifenthrin
Carbaryl
*Carbendazim
Chlormequat (expressed as cation)
Chlorothanlonil
*Chlorpyrifos
*Chlorpyrifos-methyl
*Cypermethrin
*Cyproconazole
*Deltamethrin
Diazinon
*Difenoconazole
*Endosulfan (α + ß + Sulphate expressed as Endosulfan)
Endosulfan α
Endosulfan β
Endosulfan sulphate
*Epoxiconazole
Fenhexamid
*Fenpropimorph
Fluquinconazole
Glyphosate
*Imazalil
*Iprodione
*Kresoxim-methyl
*Lambda-cyhalothrin
*Lindane (gamma-HCH)
*Malathion (Malathion + Malaoxon,expressed as Malathion)
Malathion
Malaoxon
Mepiquat (expressed as cation)
Metconazole
*Methacrifos
*Methomyl (Methomyl + Thiodicarb,expressed as Methomyl)
Methomyl
Thiodicarb
*Parathion (only parent compound)
*Penconazole
*Permethrin
*Pirimicarb
*Pirimiphos-methyl
*Prochloraz (only parent compound)
*Procymidone
*Propiconazole
Spiroxamine
*Tebuconazole
*Thiabendazole
*Thiophanate-methyl
Triadimefon (Triadimefon + Triadimenol express. as Triadimefon)
Triadimefon
Triadimenol

Field treatment of wheat – incurred pesticides

- Faculty of Agricultural Sciences, University of Aarhuss

Active substance	Application time	Produkt	Dose	MRL	Target conc. mg/kg	Residue
Chlormequat	60-80 days before harvest	Cycocel 750	300 g as/ha	2	0.10	0.217
Alpha-cypermethrin	20-30 days before harvest	Fastac 50	500g as/ha	0.05	0.1	0.079
Bifentrin	20-30 days before harvest		500 as/ha	0.5	0.2	0.087
Carbendazim	20-30 days before harvest	Bavistin DF	2000 as/ha	0.1	0.2	0.57
Difenconazole	20-30 days before harvest	Score	500g as/ha	0.02 (barley)	0.2	-
Epoxiconazole	20-30 days before harvest	Opus	1000 as/ha	0.05	0.2	0.176
Iprodione	20-30 days before harvest	Rovral	1000 as/ha	0.5	0.1	0.289
Pirimicarb	20-30 days before harvest	Pirimor G	2500 as/ha	0.05	0.5	0.038
Prochloraz	20-30 days before harvest	Sportak 45	2000 as/ha	0.5	0.5	-
Spiroxamin	20-30 days before harvest	Impulse	2500 as/ha	0.05	0.5	0.075
Trifloxystrobin	20-30 days before harvest	Flint	2500 as/ha	0.05	0.5	0.439
Chlorpyrifos-methyl	3-5 days before harvest	Reldan 22	5000g as/ha	3	0.5	0.033
Glyphosate	3-5 days before harvest	Roundup	3000 as/ha	10	0.5	1.93
Malathion	3-5 days before harvest		1500 as/ha	8	0.5	-

Spiking of wheat

- 4 times 1 kg wheat were spike with 4 different pesticides

Active substance	Produkt	MRL	Target conc. mg/kg	Residue
Difenconazole	Score	0.02	0.2	0.169
Malathion		8	0.2	0.162
Prochloraz	Sportak 45	0.5	0.2	0.239
Azoxystrobin	Amistar	0.3	0.2	0.239

- The spiked wheat was mixed with 56 kg of wheat with incurred pesticides

Homogeniety

	Azoxystrobin	Alfa-cypermethrin	Bifenthrin	Carbendazim	Chlropyriphos-methyl	Chlormequat	Difenconazole	Epoxyconazole
Mean (mg/kg)	0.240	0.089	0.114	0.703	0.132	0.192	0.177	0.175
Ss/σ	0.084	0.203	0.254	0.062	0.238	0.102	0.144	0.267
Pass/Fail	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass

	Glyphosate	Iprodion	Malathion	Pirimicarb	Prochloraz	Spiroxamine	Trifloxystrobin
Mean (mg/kg)	2.17	0.313	0.167	0.042	0.233	0.049	0.484
Ss/σ	0.018	0.251	0.12	0.235	0.077	0.227	0.234
Pass/Fail	Pass	Pass	Pass	Pass	Pass	Pass	Pass

Stability

	Azoxystrobin	Alfa-cypermethrin	Bifenthrin	Carbendazim	Chlorpyriphos-methyl	Chlormequat	Difenconazole	Epoxyconazole
Day 1 (mean)	0.261	0.094	0.114	0.703	0.134	0.191	0.173	0.185
Day 2 (mean)	0.264	0.097	0.117	0.712	0.139	0.206	0.173	0.186
%	1%	4%	3%	1%	3%	8%	0%	1%

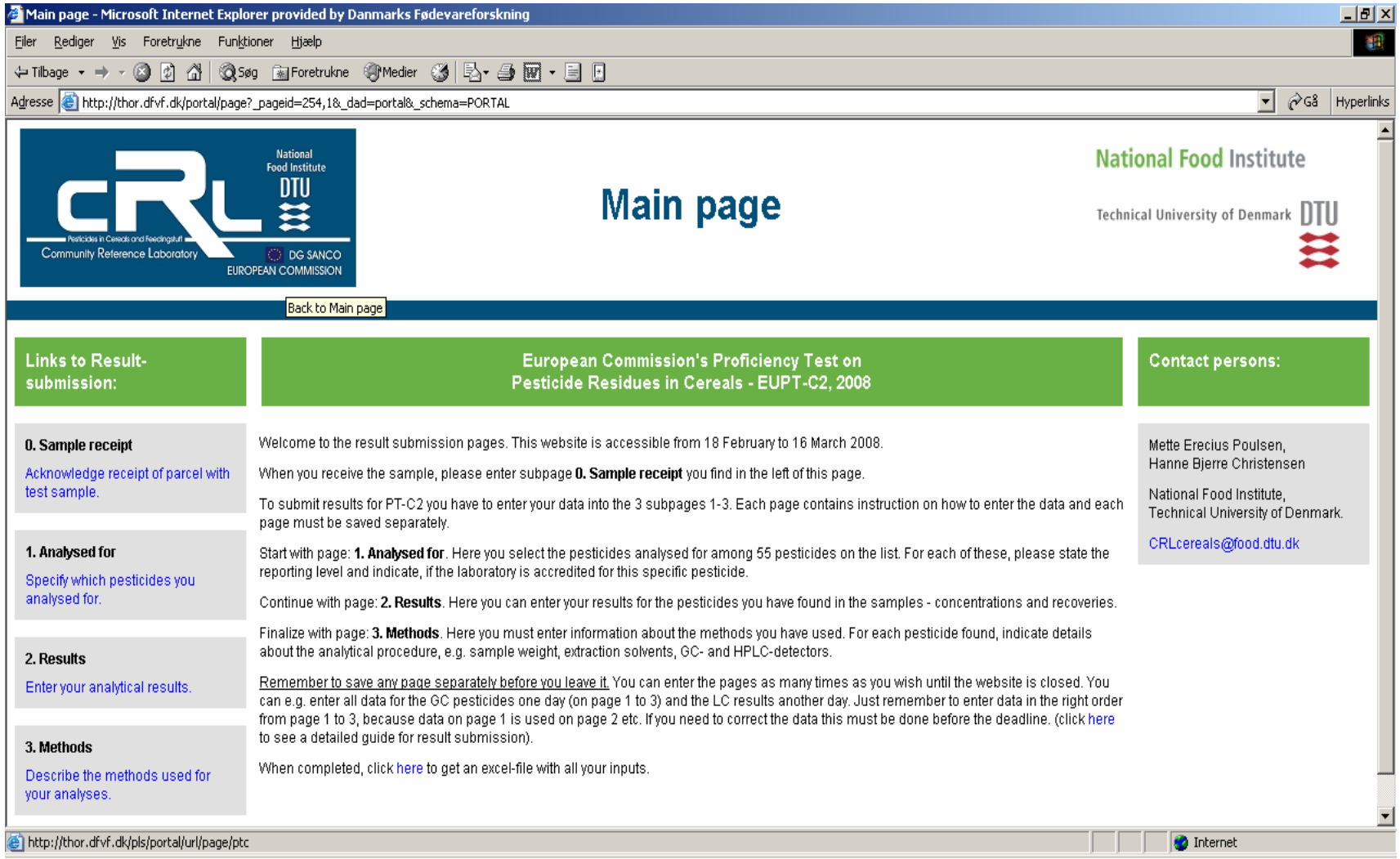
	Glyphosate	Iprodion	Malathion	Pirimicarb	Prochloraz	Spiroxamine	Trifloxystrobin
Day 1 (mean)	2.17	0.327	0.139	0.040	0.247	0.050	0.511
Day 2 (mean)	2.26	0.351	0.144	0.041	0.252	0.056	0.520
%	4%	7%	3%	3%	2%	3%	2%

Sample shipment

- Fedex
- Samples were distributed on Monday 18 February
- Most samples were delivered on 19 or 20 February
- All samples were delivered before 22 February

Result submission

- http://thor.dfvf.dk/ptc2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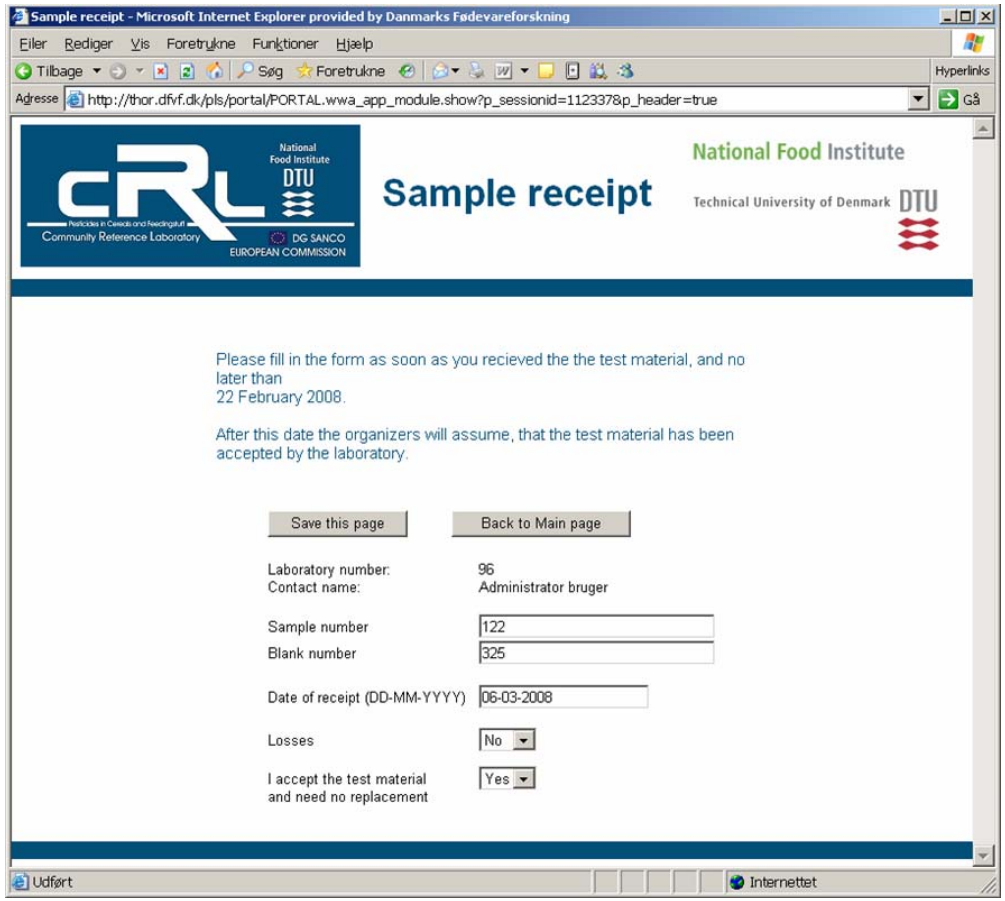
Gå Hyperlinks
National Food Institute DTU
Pesticides in Cereals and Feedingstuff
Community Reference Laboratory
DG SANCO
EUROPEAN COMMISSION
Main page
National Food Institute
Technical University of Denmark DTU
Back to Main page
Links to Result-submission:
European Commission's Proficiency Test on Pesticide Residues in Cereals - EUPT-C2, 2008
Contact persons:
0. Sample receipt
Acknowledge receipt of parcel with test sample.
1. Analysed for
Specify which pesticides you analysed for.
2. Results
Enter your analytical results.
3. Methods
Describe the methods used for your analyses.
Welcome to the result submission pages. This website is accessible from 18 February to 16 March 2008.
When you receive the sample, please enter subpage 0. Sample receipt you find in the left of this page.
To submit results for PT-C2 you have to enter your data into the 3 subpages 1-3. Each page contains instruction on how to enter the data and each page must be saved separately.
Start with page: 1. Analysed for. Here you select the pesticides analysed for among 55 pesticides on the list. For each of these, please state the reporting level and indicate, if the laboratory is accredited for this specific pesticide.
Continue with page: 2. Results. Here you can enter your results for the pesticides you have found in the samples - concentrations and recoveries.
Finalize with page: 3. Methods. Here you must enter information about the methods you have used. For each pesticide found, indicate details about the analytical procedure, e.g. sample weight, extraction solvents, GC- and HPLC-detectors.
Remember to save any page separately before you leave it. You can enter the pages as many times as you wish until the website is closed. You can e.g. enter all data for the GC pesticides one day (on page 1 to 3) and the LC results another day. Just remember to enter data in the right order from page 1 to 3, because data on page 1 is used on page 2 etc. If you need to correct the data this must be done before the deadline. (click here to see a detailed guide for result submission).
When completed, click here to get an excel-file with all your inputs.
Mette Erecius Poulsen,
Hanne Bjerre Christensen
National Food Institute,
Technical University of Denmark.
CRLcereals@food.dtu.dk
http://thor.dfvf.dk/pls/portal/url/page/ptc
Internet

Result submission



Results – overview

	No. of reported results	No. of NA	False negatives	% results
Azoxystrobin	64	8	0	89
Alpha-cypermethrin	43	21	8	60
Cypermethrin	29	12	31	40
Cypermethrin all	58	12	3	81
Bifentrin	64	7	1	89
Carbendazim	47	23	2	65
Chlormequat	26	46		36
Chlorpyrifos-methyl	69	2	1	96
Difenconazole	48	23	1	67
Epoxiconazole	45	24	3	63
Glyphosate	5	67		7
Iprodione	58	13	1	81
Malathion	65	5	2	90
Pirimicarb	43	7	22*	60
Prochloraz	54	15	3	75
Spiroxamin	51	19	2*	71
Trifloxystrobin	61	11	0	85

Results – cypermethrin/alpha-cypermethrin

	No. of reported results	No. of NA	False negatives	% results
Azoxystrobin	64	8	0	89
Alpha-cypermethrin	43	21	8	60
Cypermethrin	29	12	31	40
Cypermethrin all	58	12	4	81
Bifentrin	64	7	1	89
Carbendazim	47	23	2	65
Chlormequat	26	46		36
Chlorpyrifos-methyl	69	2	1	96
Difenconazole	48	23	1	67
Epoxiconazole	45	24	3	63
Glyphosate	5	67		7
Iprodione	58	13	1	81
Malathion	65	5	2	90
Pirimicarb	43	7	22*	60
Prochloraz	54	15	3	75
Spiroxamin	51	19	2*	71
Trifloxystrobin	61	11	0	85

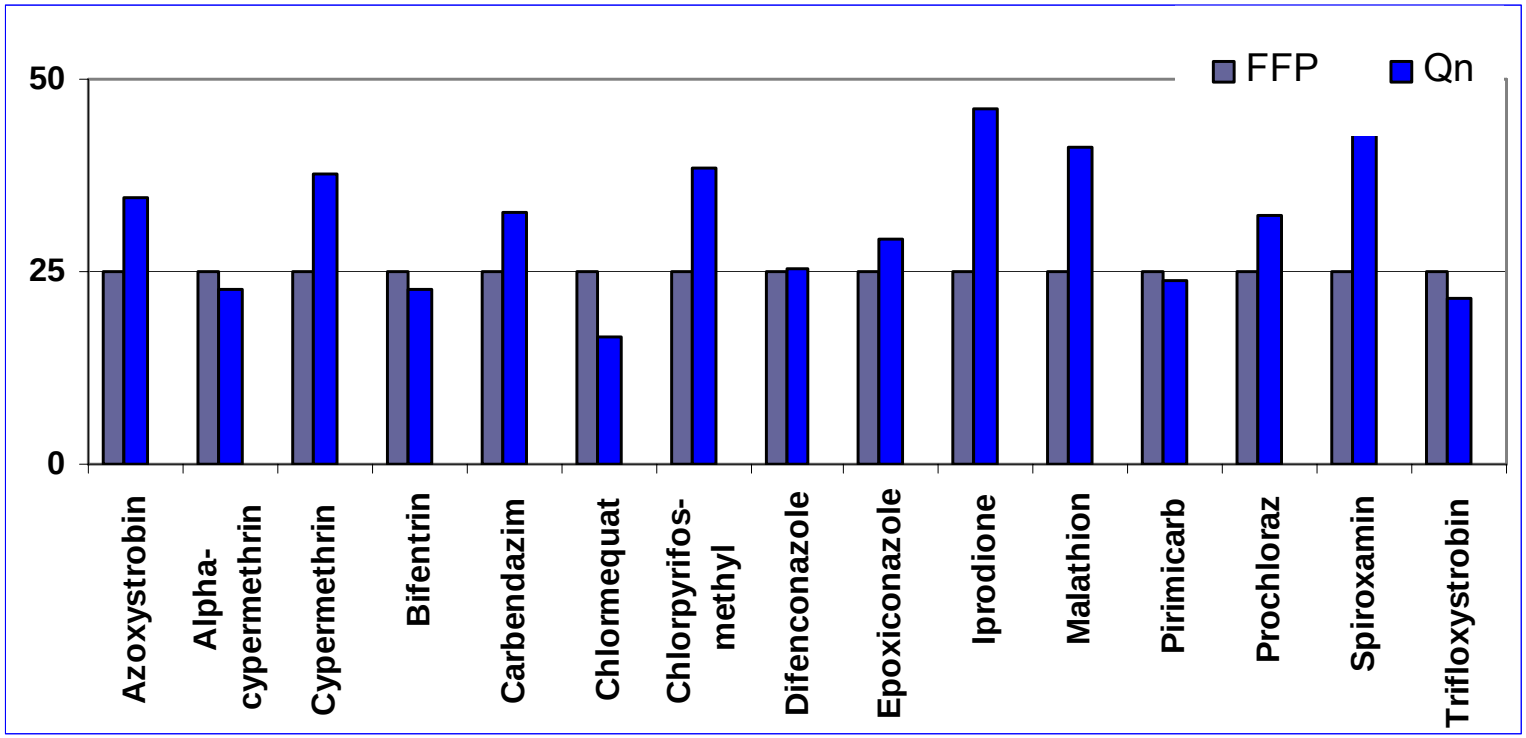
Results – high number of NA

	No. of reported results	No. of NA	False negatives	% results
Azoxystrobin	64	8	0	89
Alpha-cypermethrin	43	21	8	60
Cypermethrin	29	12	31	40
Cypermethrin all	58	12	3	81
Bifentrin	64	7	1	89
Carbendazim	47	23	2	65
Chlormequat	26	46		36
Chlorpyrifos-methyl	69	2	1	96
Difenconazole	48	23	1	67
Epoxiconazole	45	24	3	63
Glyphosate	5	67		7
Iprodione	58	13	1	81
Malathion	65	5	2	90
Pirimicarb	43	7	22*	60
Prochloraz	54	15	3	75
Spiroxamin	51	19	2*	71
Trifloxystrobin	61	11	0	85

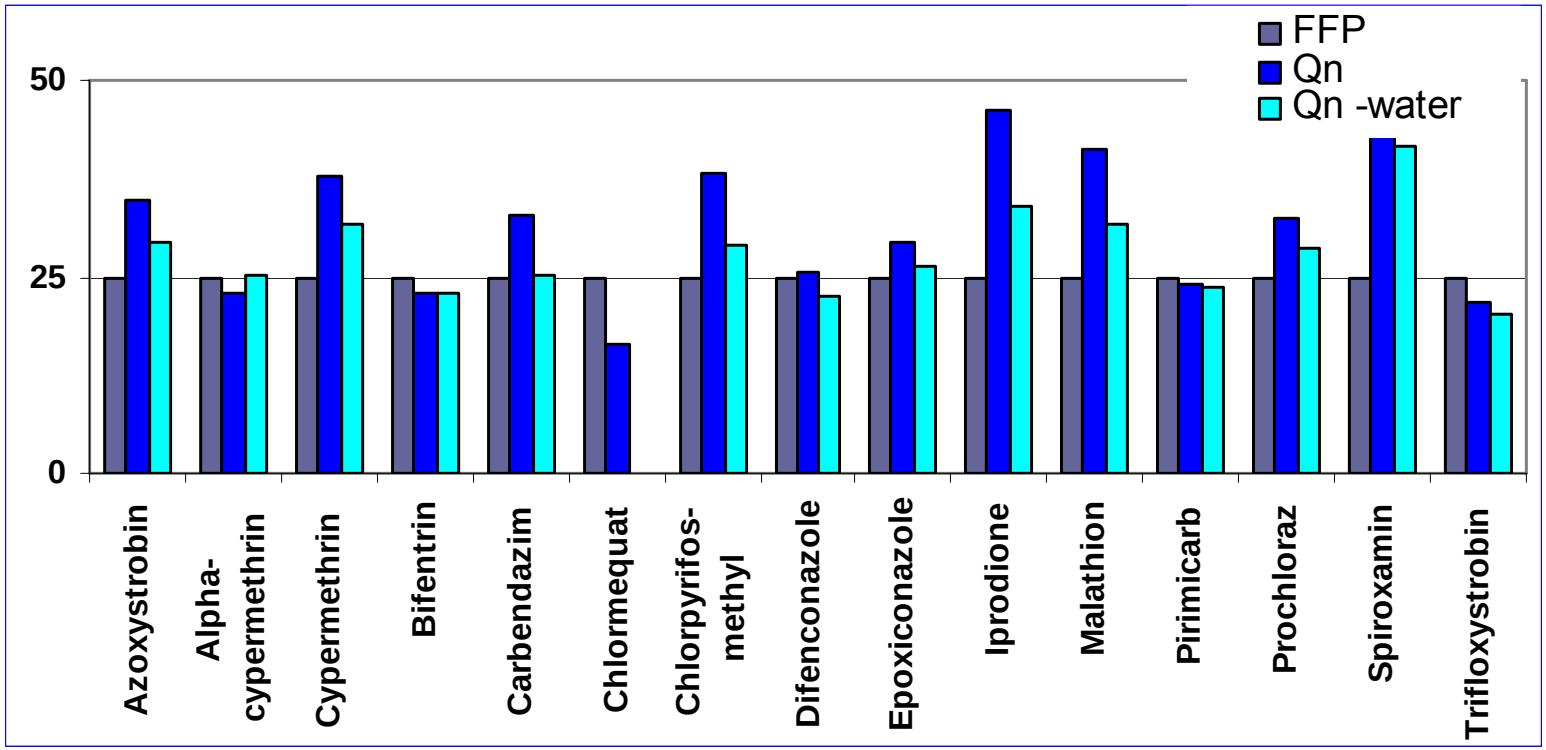
Results – low number of reported result and low assigned value

	No. of reported results	No. of NA	False negatives	% results
Azoxystrobin	64	8	0	89
Alpha-cypermethrin	43	21	8	60
Cypermethrin	29	12	31	40
Cypermethrin all	58	12	3	81
Bifentrin	64	7	1	89
Carbendazim	47	23	2	65
Chlormequat	26	46		36
Chlorpyrifos-methyl	69	2	1	96
Difenconazole	48	23	1	67
Epoxiconazole	45	24	3	63
Glyphosate	5	67		7
Iprodione	58	13	1	81
Malathion	65	5	2	90
Pirimicarb	43	7	22*	60
Prochloraz	54	15	3	75
Spiroxamin	51	19	2*	71
Trifloxystrobin	61	11	0	85

FFP (25%) versus Qn – all result

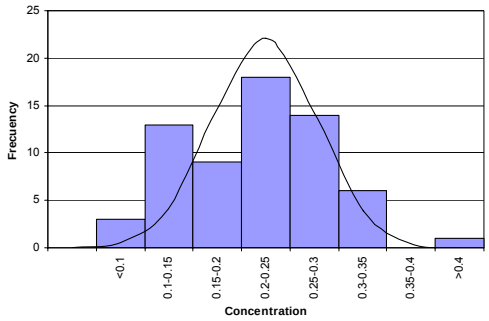


FFP (25%) versus Qn – water

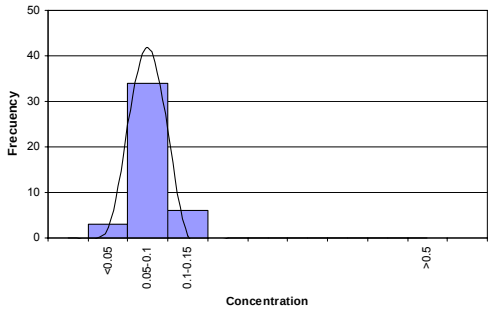


Distributions

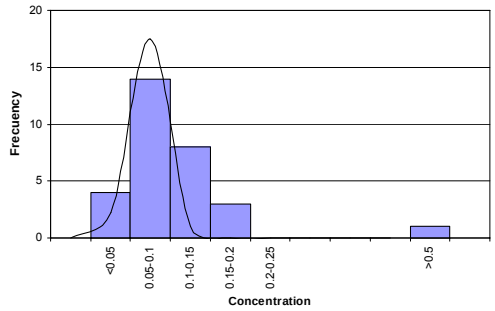
Azoxystrobin



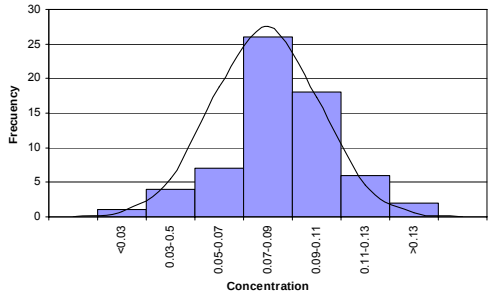
Alpha-cypermethrin



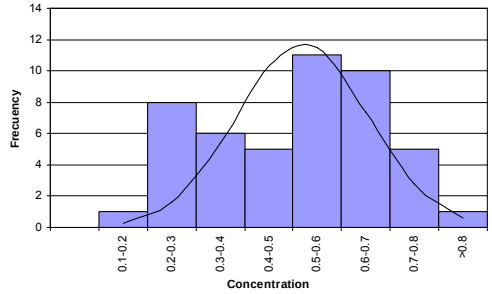
Cypermethrin



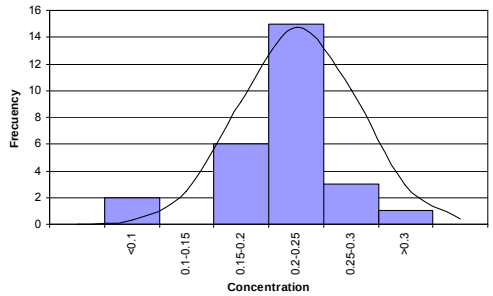
Bifenthrin



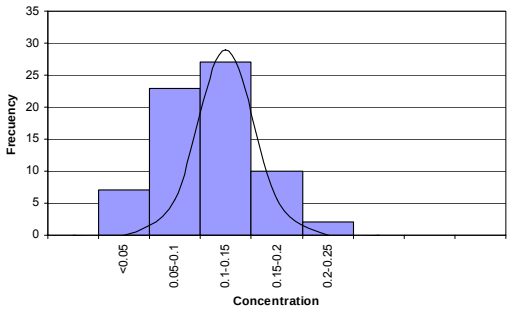
Carbendazim



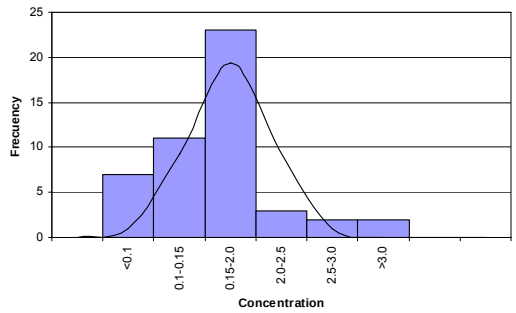
Chlormequat



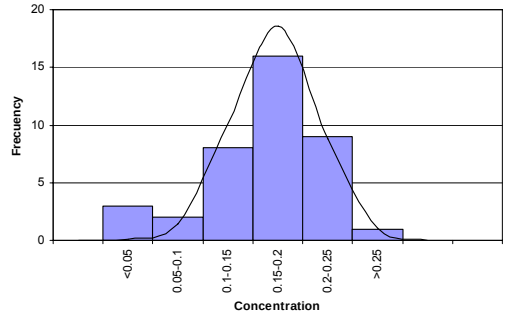
Chlorpyrifos-methyl



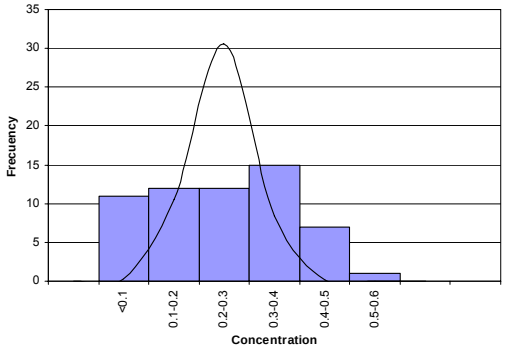
Difenoconazole



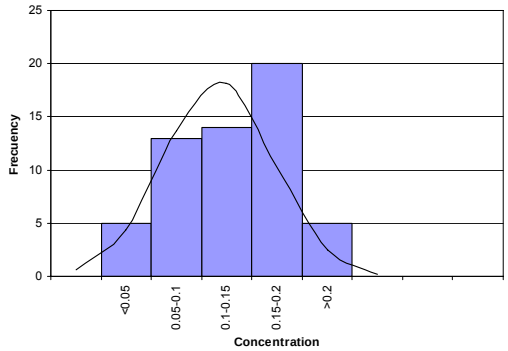
Epoxiconazole



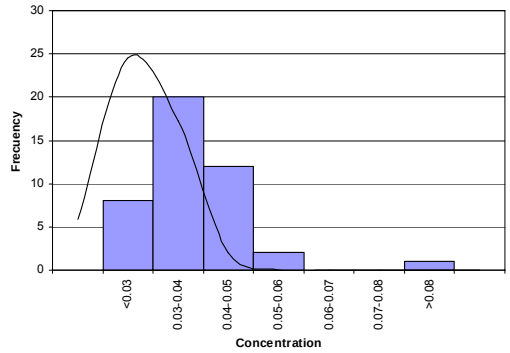
Iprodione



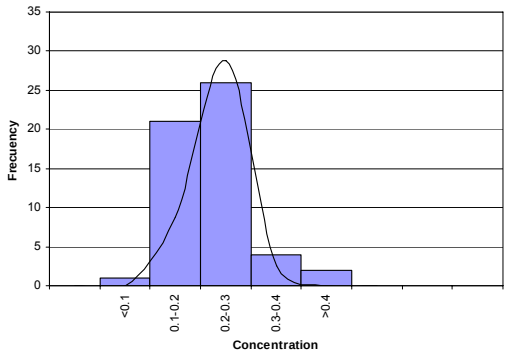
Malathion



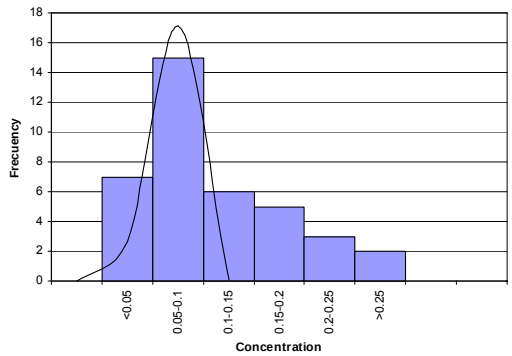
Pirimicarb



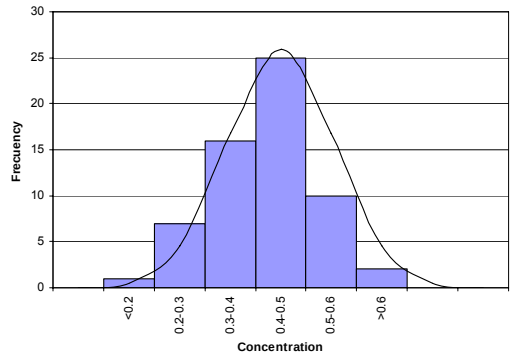
Prochloraz



Spiroxamin



Trifloxostrobin



False positives

Lab no.		MRRL	Reported results	Reporting limit from lab	False positive
ptc213	Vinclozolin	0.05	0.01	0.01	no
	malaoxon	0.05	0.01	0.01	no
ptc210	Lindane	0.01	0.0002	0.0002	no
	Endosulfane	0.02	0.0003	-	no
	Endosulfane- alpha	0.02	0.0003	0.0003	no
	Diazinon	0.02	0.003	0.0003	no
	Chlorpyrifos	0.02	0.0001	0.0001	no
ptc237	Fenhexamid	0.05	0.074	0.05	yes
ptc238	Fenhexamid	0.05	0.056	0.05	yes

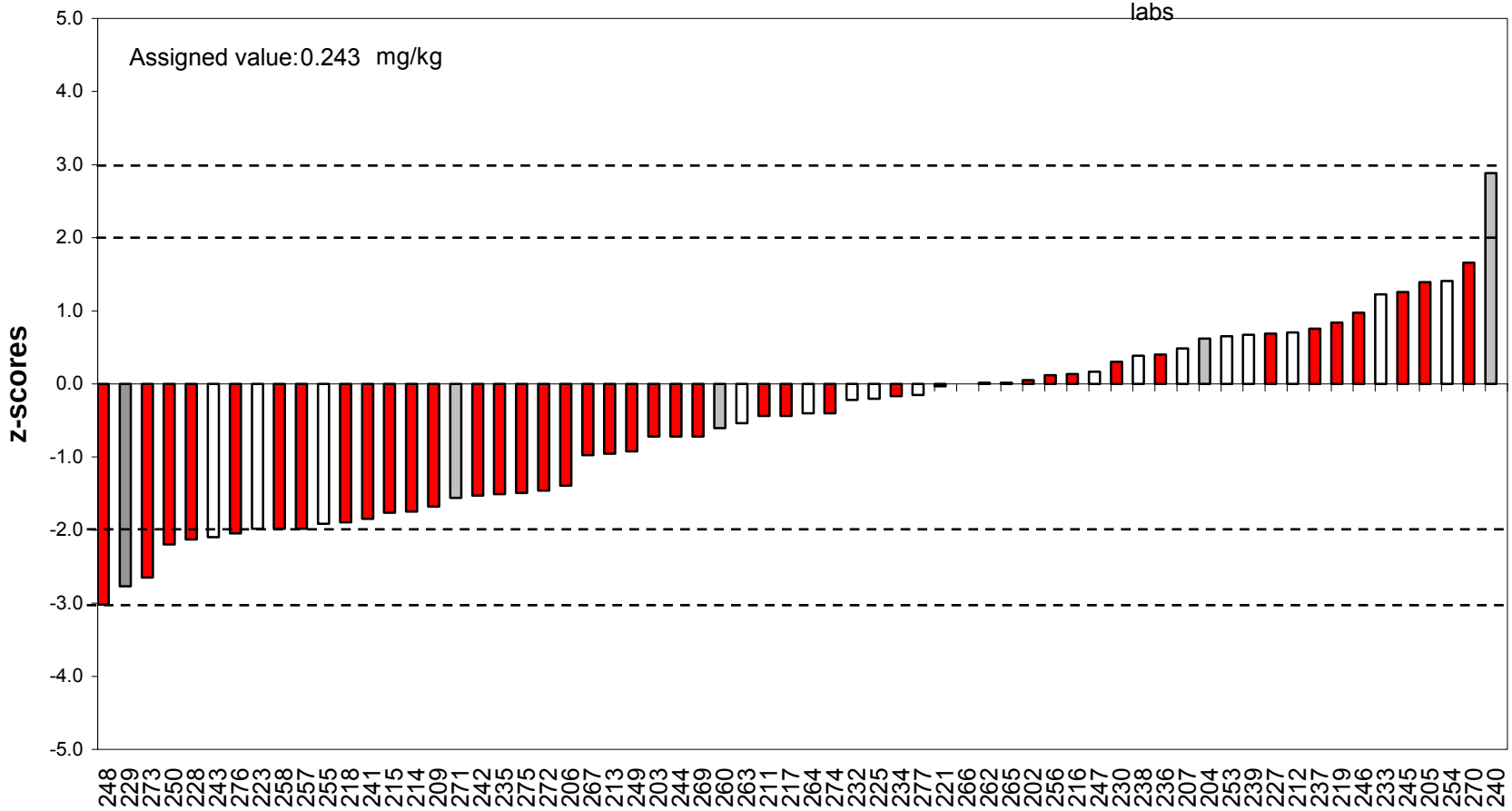
False negatives

	No. of false Negatives	MRRL	Assigned Value	Resulting z-score
Azoxystrobin	0	0.02	0.239	-3.7
Bifentrin	1	0.02	0.087	-3.1
(Alpha-)cypermethrin	4	0.02	0.079	-3
Carbendazim	2	0.02	0.570	-3.9
Chlormequat	0	0.05	0.217	-3.1
Chlorpyrifos-methyl	1	0.02	0.130	-3.4
Difenconazole	1	0.05	0.169	-2.8
Epoxiconazole	3	0.05	0.176	-2.9
Iprodione	1	0.02	0.289	-3.7
Malathion	4	0.05	0.168	-2.8
Pirimicarb	22	0.02	0.038	1.9
Prochloraz	3	0.05	0.239	-3.2
Spiroxamin	2	0.05	0.075	-1.3
Trifloxystrobin	0	0.05	0.439	-3.5

Azoxystrobin
LC/GC

or 1: LC
or 2: GC
or 3: not specificed or both

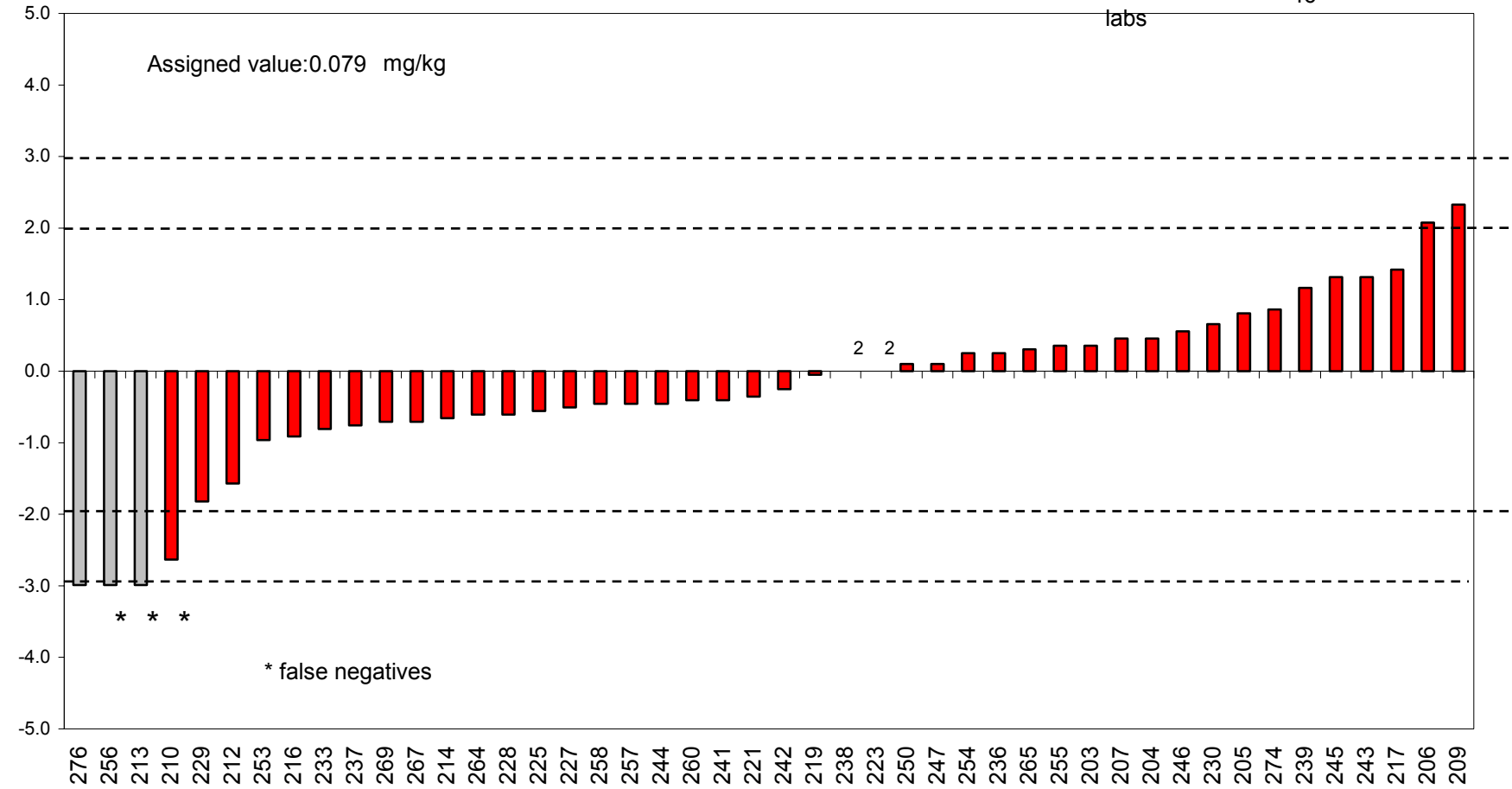
Acceptable	91%
Questionable	9%
Unacceptable	0%
Number of labs	64



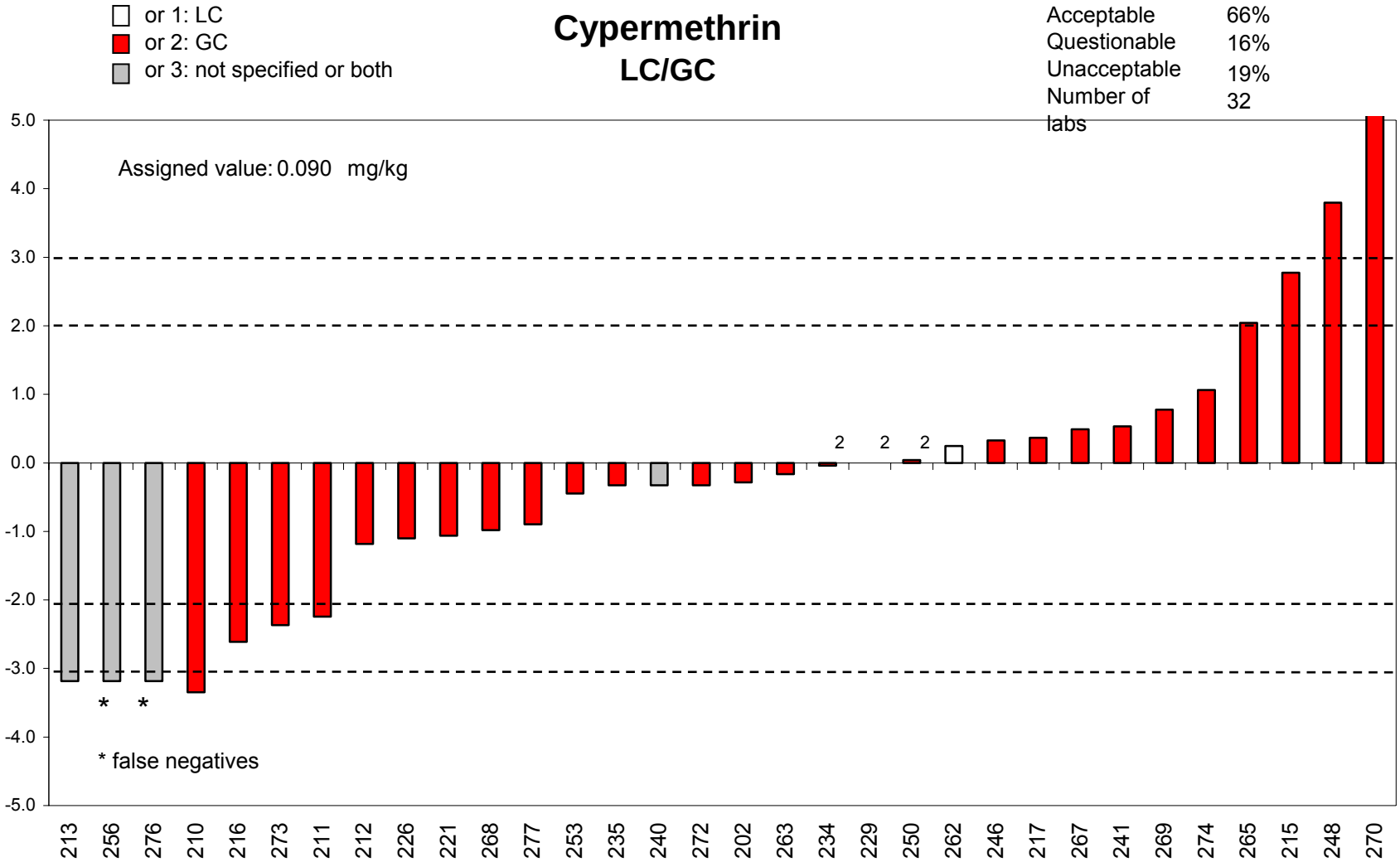
Alpha-cypermethrin
LC/GC

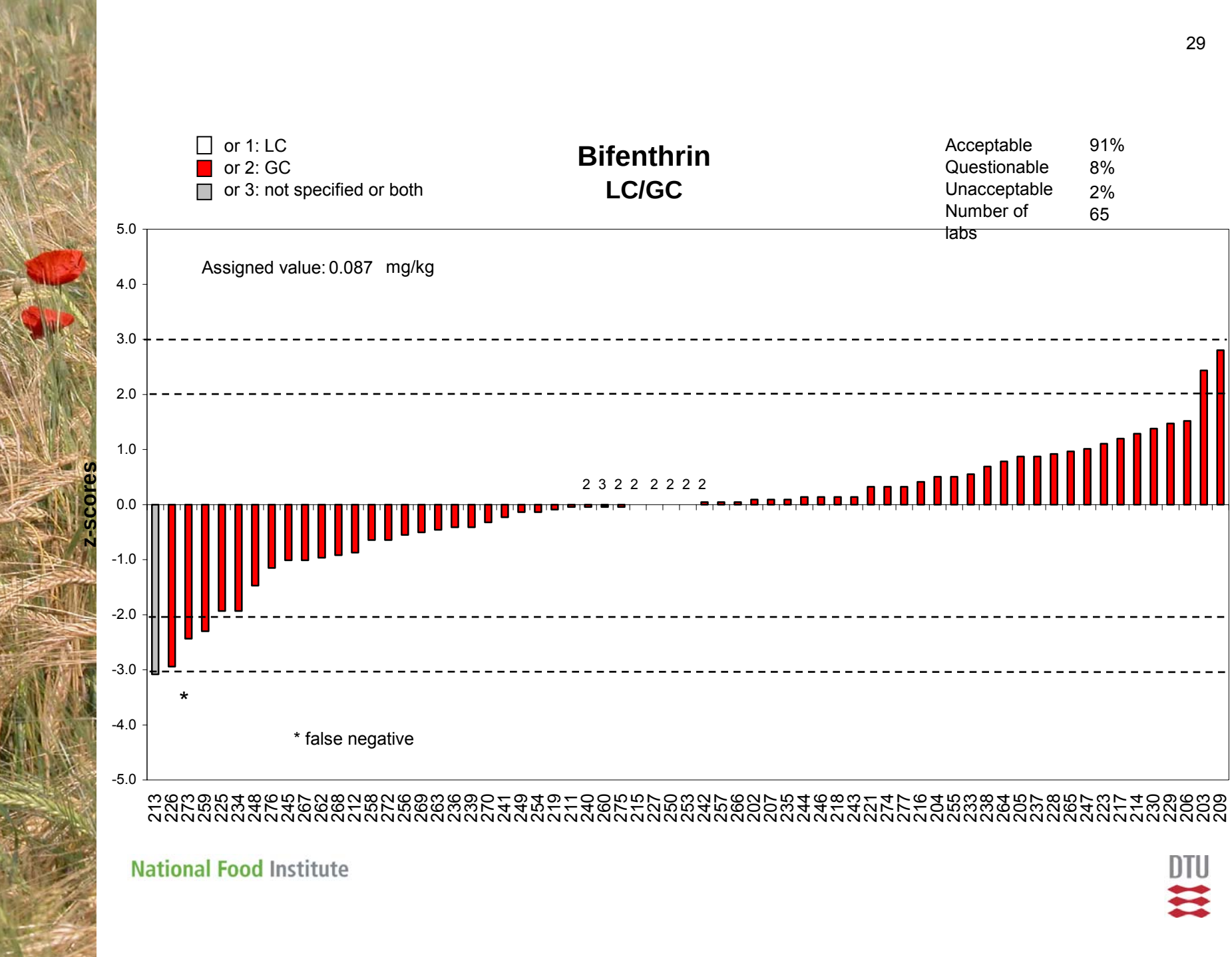
or 1: LC
or 2: GC
or 3: not specificed or both

Acceptable	87%
Questionable	7%
Unacceptable	7%
Number of labs	46

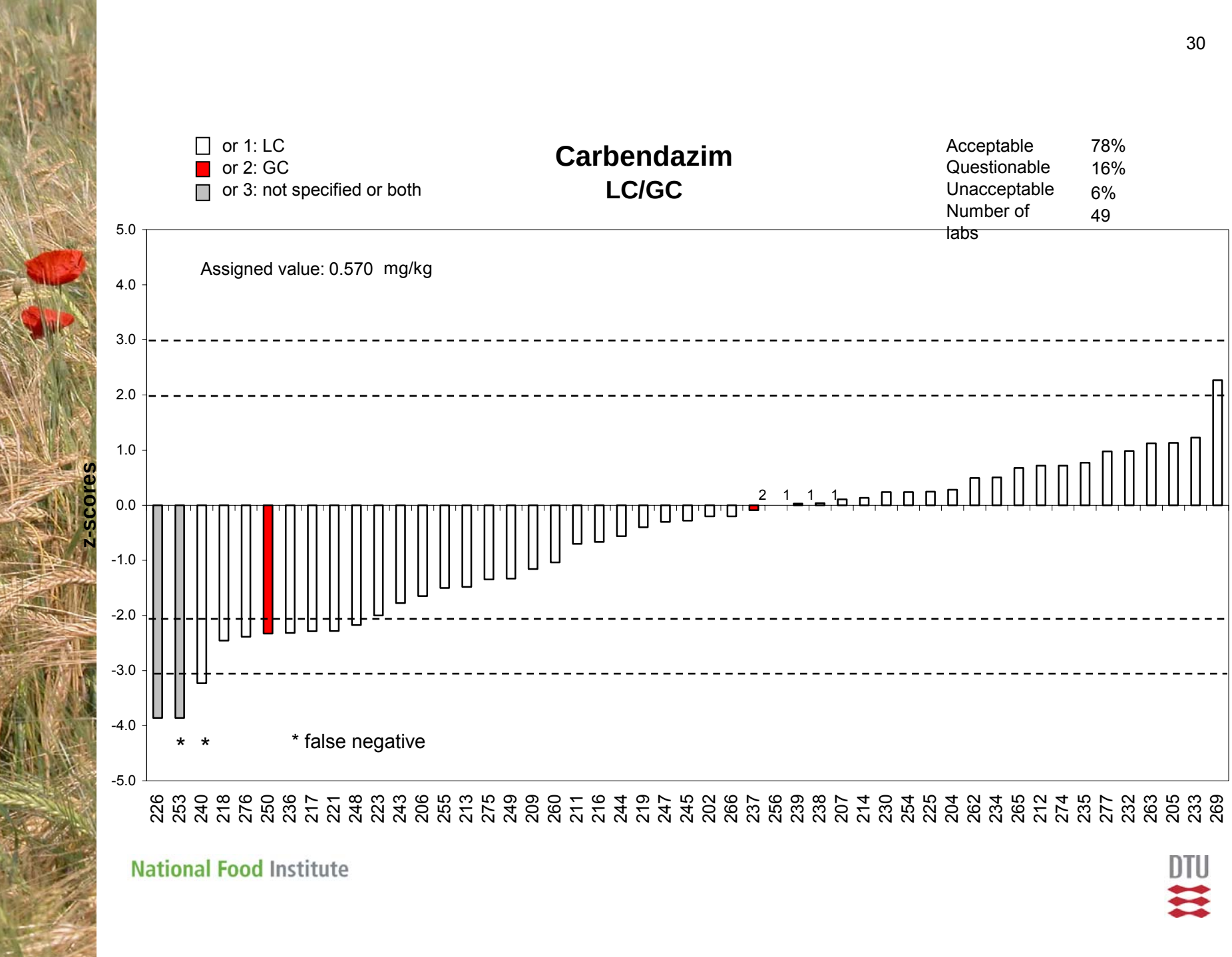


Cypermethrin
LC/GC




or 1: LC
or 2: GC
or 3: not specified or both
Bifenthrin
LC/GC
Acceptable 91%
Questionable 8%
Unacceptable 2%
Number of labs 65
Assigned value: 0.087 mg/kg
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
2 3 2 2 2 2 2 2
*
* false negative
213 226 273 259 225 234 248 276 245 267 262 268 212 258 272 256 269 263 236 239 270 241 249 254 219 211 240 260 275 215 227 250 253 242 257 266 202 207 235 244 246 218 243 221 274 277 216 204 255 233 238 264 205 237 228 265 247 223 217 214 230 229 206 203 209

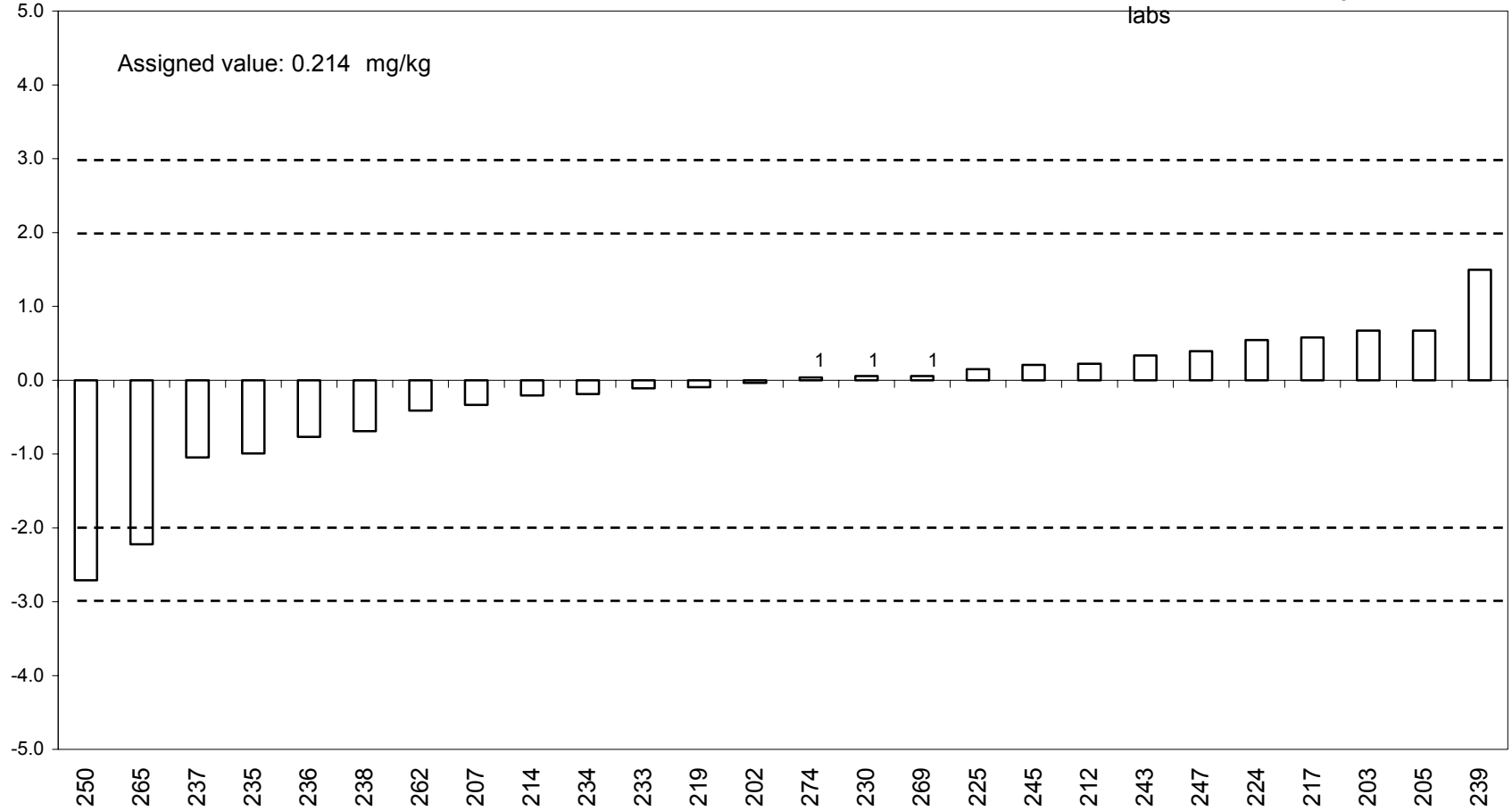
Carbendazim
LC/GC



Chlormequat
LC/GC

or 1: LC
or 2: GC
or 3: not specified or both

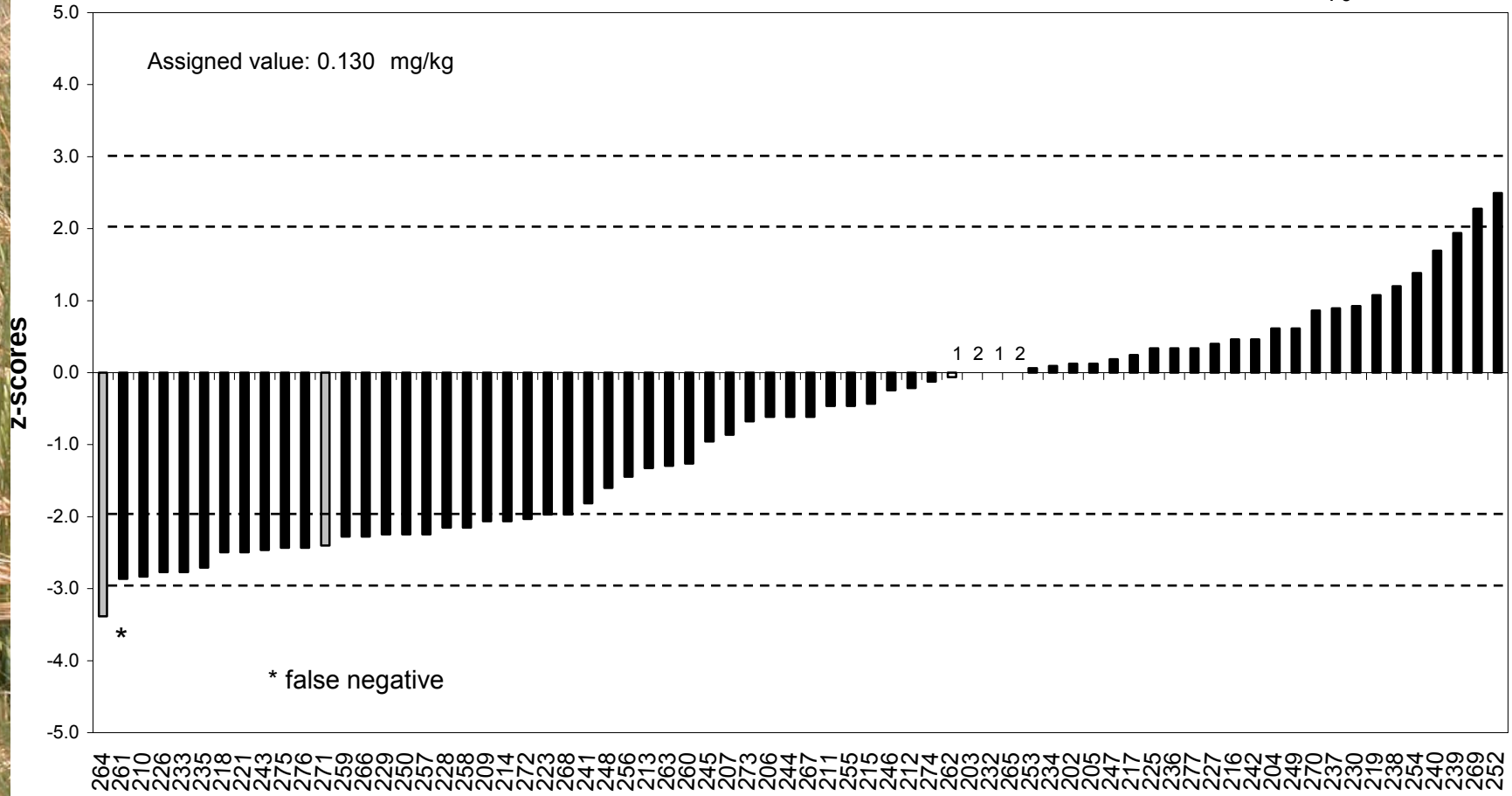
Acceptable	92%
Questionable	8%
Unacceptable	0%
Number of labs	26



Chlorpyrifos-methyl

or 1: LC
or 2: GC
or 3: not specified or both

Acceptable	66%
Questionable	33%
Unacceptable	1%
Number of labs	70



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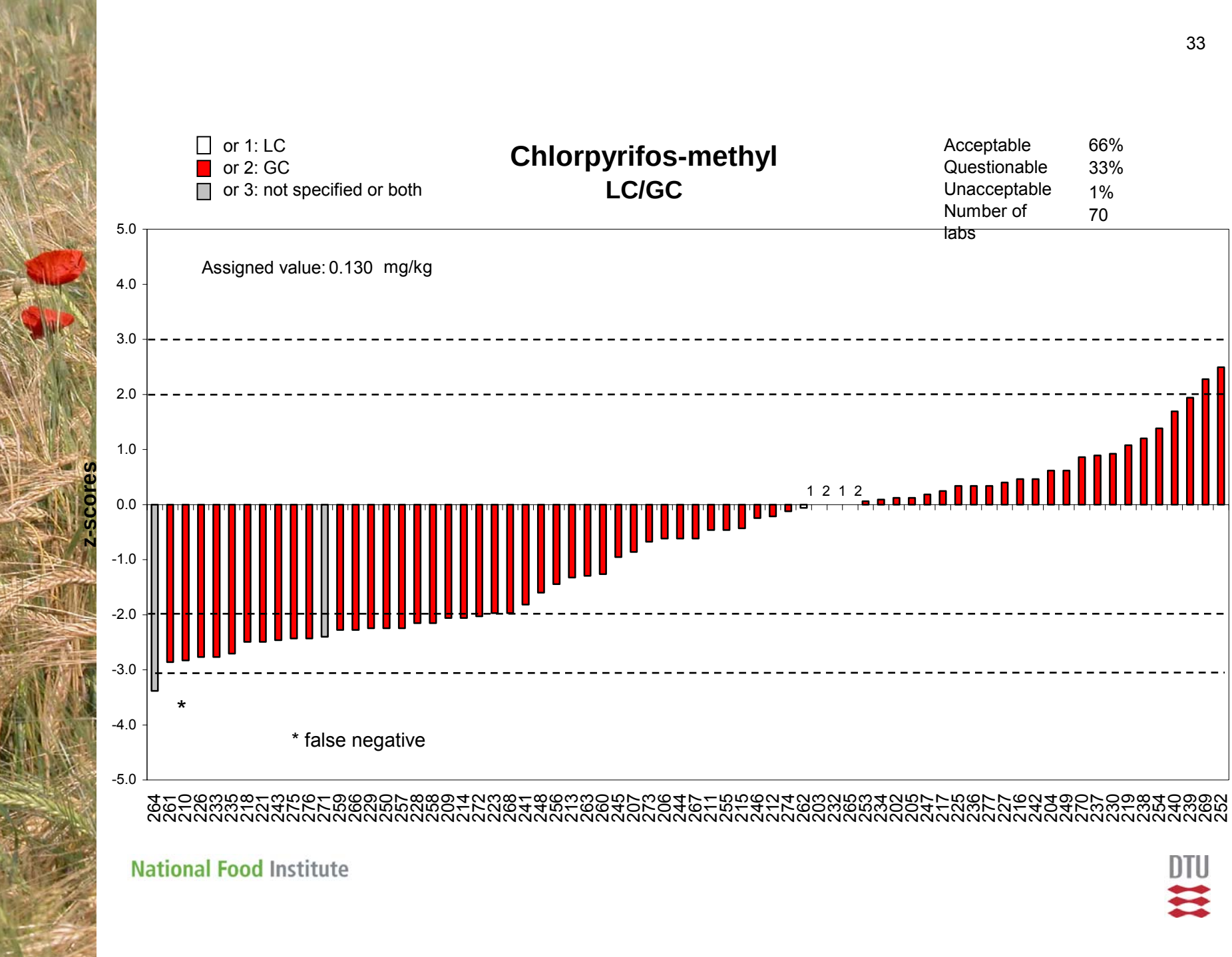

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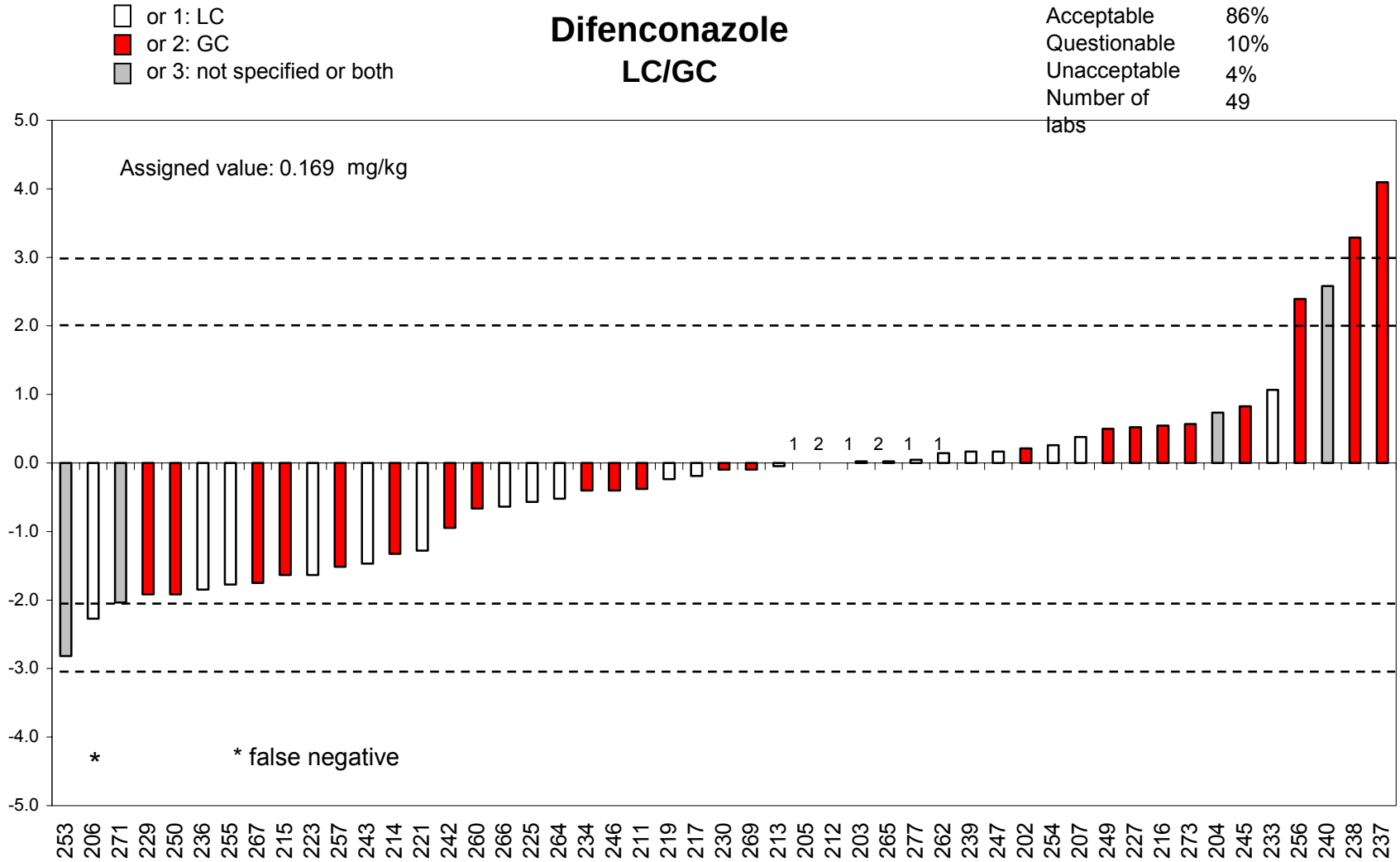
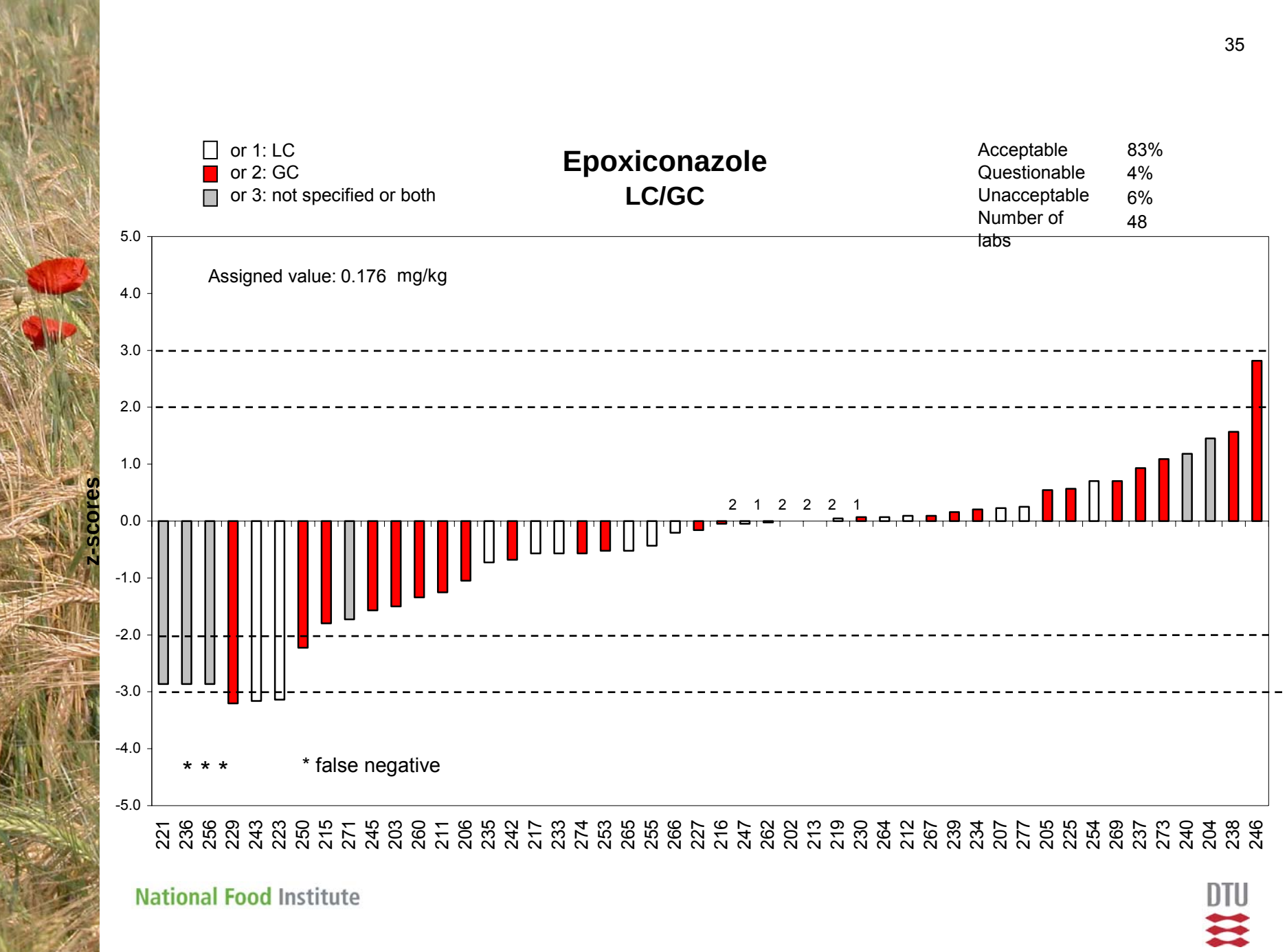
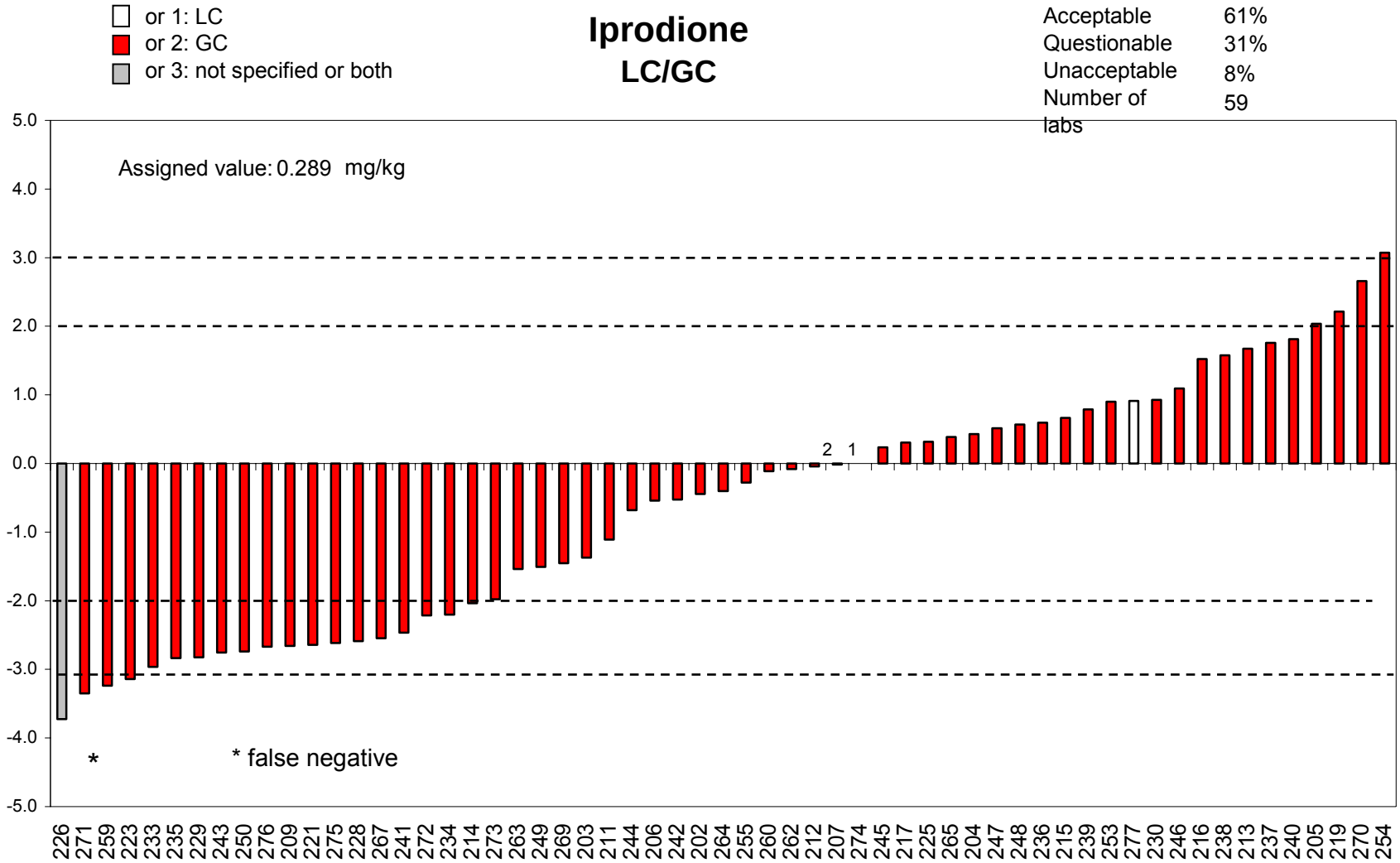
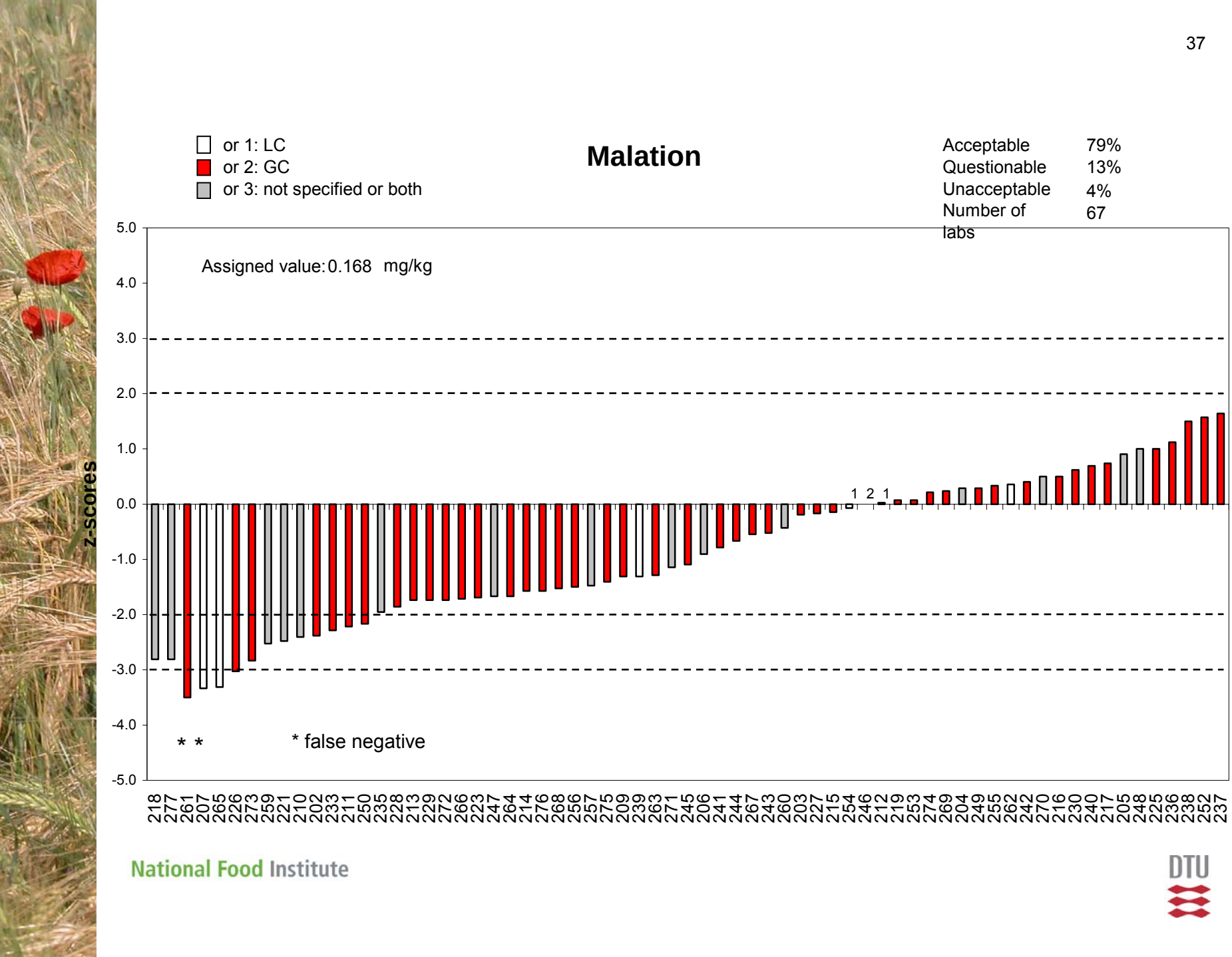
Difenconazole
LC/GC

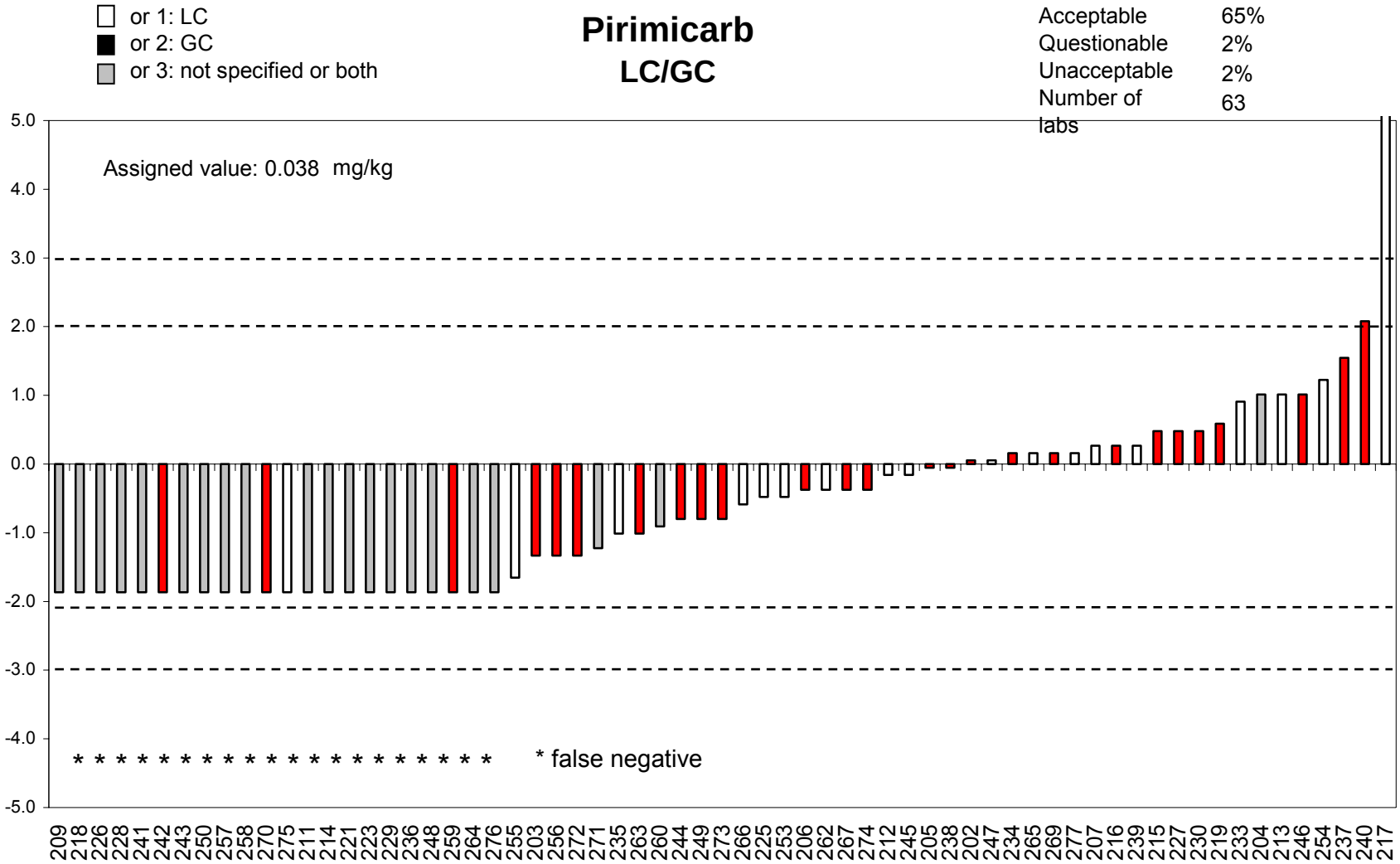



or 1: LC
or 2: GC
or 3: not specified or both
Epoxiconazole
LC/GC
Acceptable 83%
Questionable 4%
Unacceptable 6%
Number of labs 48
Assigned value: 0.176 mg/kg
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
2 1 2 2 2 1
* * *
* false negative
221 236 256 229 243 223 250 215 271 245 203 260 211 206 235 242 217 233 274 253 265 255 266 227 216 247 262 202 213 219 230 264 212 267 239 234 207 277 205 225 254 269 237 273 240 204 238 246

Iprodione
LC/GC



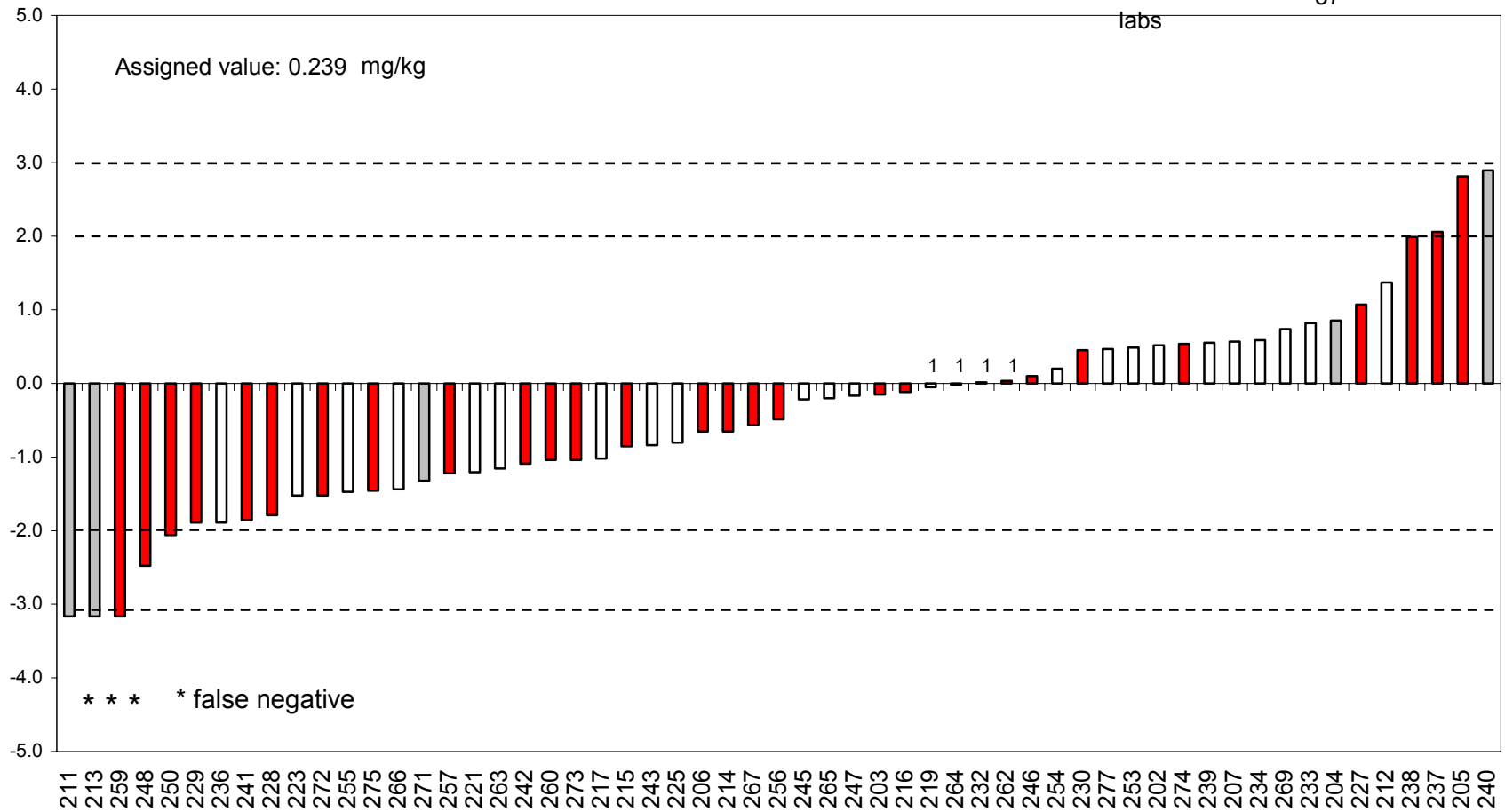

or 1: LC
or 2: GC
or 3: not specified or both
Malation
Acceptable 79%
Questionable 13%
Unacceptable 4%
Number of labs 67
Assigned value: 0.168 mg/kg
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
1 2 1
* *
* false negative
218 277 261 207 265 226 273 259 221 210 202 233 211 250 235 228 213 229 272 266 223 247 264 214 276 268 256 257 275 209 239 263 271 245 206 241 244 267 243 260 203 227 215 254 246 212 219 253 274 269 204 249 255 262 242 270 216 230 240 217 205 248 225 236 238 252 237


or 1: LC
or 2: GC
or 3: not specified or both
Pirimicarb
LC/GC
Acceptable 65%
Questionable 2%
Unacceptable 2%
Number of labs 63
Assigned value: 0.038 mg/kg
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
* * * * * * * * * * * * * * * * * * * *
* false negative
209 218 226 228 241 242 243 250 257 258 270 275 211 214 221 223 229 236 248 259 264 276 255 203 256 272 271 235 263 260 244 249 273 266 225 253 206 262 267 274 212 245 205 238 202 247 234 265 269 277 207 216 239 215 227 230 219 233 204 213 246 254 237 240 217

Procloraz
LC/GC

or 1: LC
or 2: GC
or 3: not specified or both

Acceptable	86%
Questionable	9%
Unacceptable	5%
Number of labs	57



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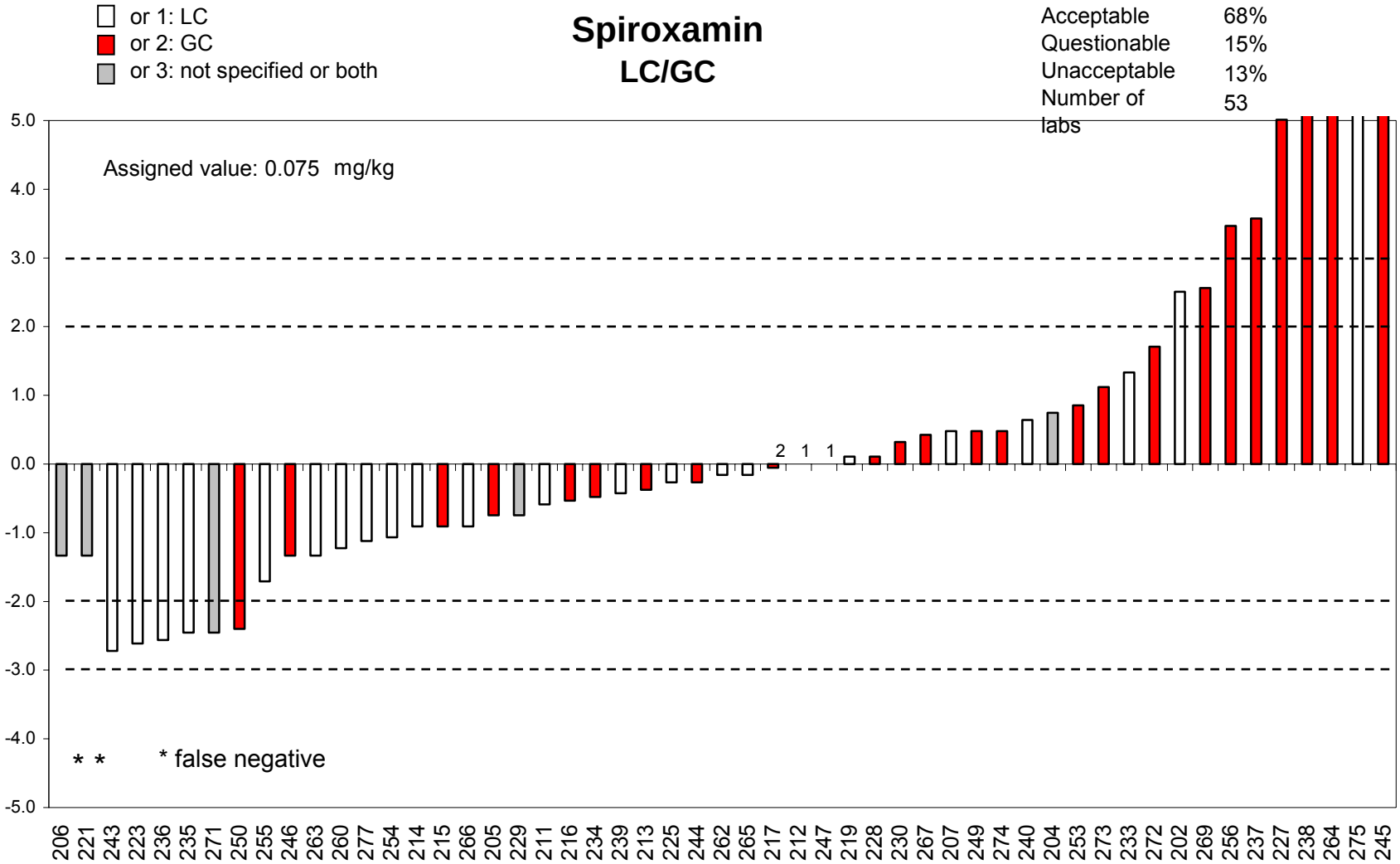
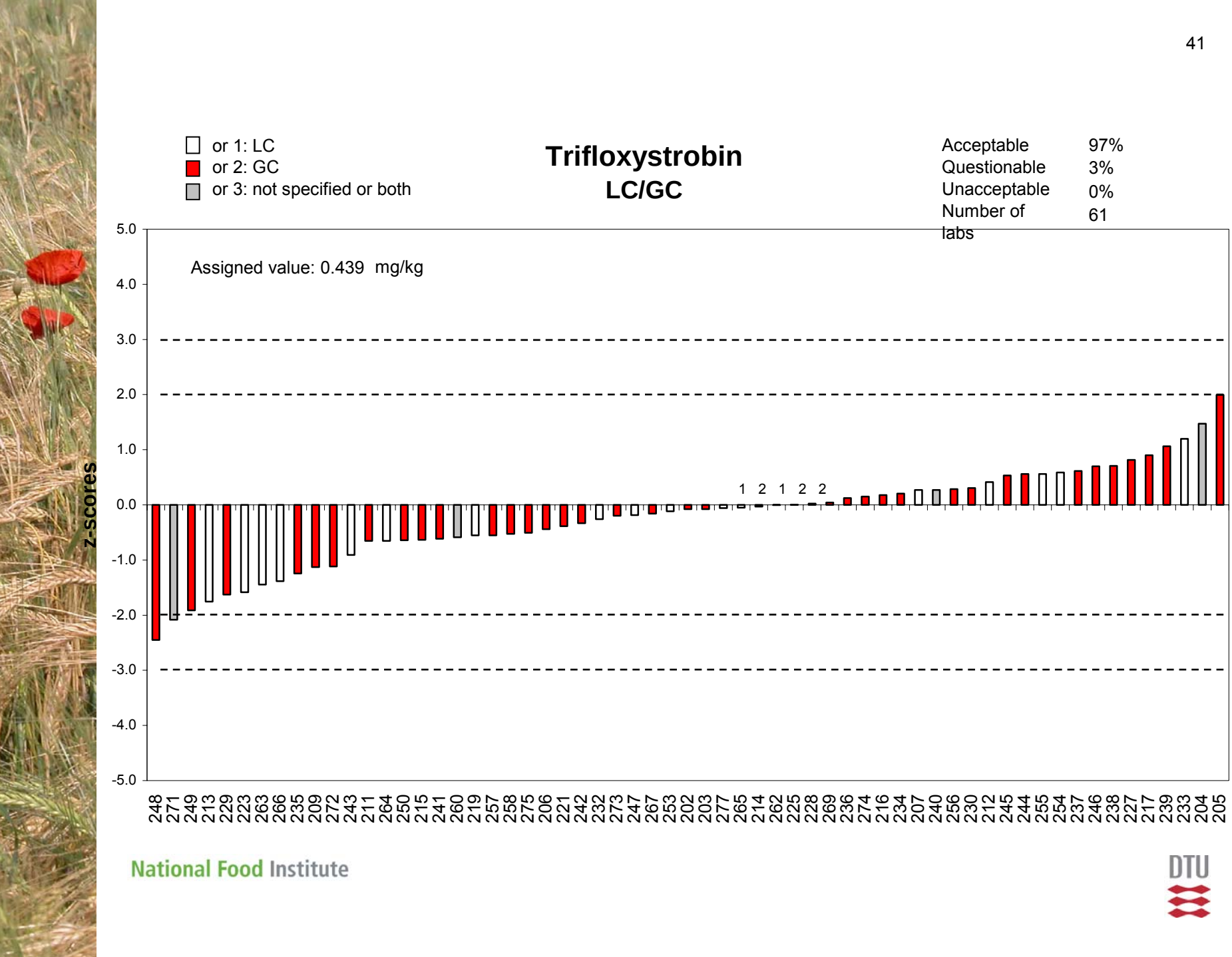

or 1: LC
or 2: GC
or 3: not specified or both
Spiroxamin
LC/GC
Acceptable 68%
Questionable 15%
Unacceptable 13%
Number of labs 53
Assigned value: 0.075 mg/kg
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
2 1 1
* *
* false negative
206 221 243 223 236 235 271 250 255 246 263 260 277 254 214 215 266 205 229 211 216 234 239 213 225 244 262 265 217 212 247 219 228 230 267 207 249 274 240 204 253 273 233 272 202 269 256 237 227 238 264 275 245


or 1: LC
or 2: GC
or 3: not specified or both
Trifloxystrobin
LC/GC
Acceptable 97%
Questionable 3%
Unacceptable 0%
Number of labs 61
Assigned value: 0.439 mg/kg
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
1 2 1 2 2
248 271 249 213 229 223 263 266 235 209 272 243 211 264 250 215 241 260 219 257 258 275 206 221 242 232 273 247 267 253 202 203 277 265 214 262 225 228 269 236 274 216 234 207 240 256 230 212 245 244 255 254 237 246 238 227 217 239 233 204 205
National Food Institute
DTU

Glyphosate

Lab	mg/kg
212	1.05
271	1.50
236	1.90
243	1.96
219	2.46

Results - Overview

	No. of reported results	Acceptable	Questionable	Unacceptable	False negatives
Azoxystrobin	64	57	7		0
Alpha-cypermethrir	43	40	3		8
Cypermethrin	29	21	5	3	31
Cypermethrin all	58	58			3
Bifentrin	64	59	5		1
Carbendazim	47	38	8	1	2
Chlormequat	26	24	2		
Chlorpyrifos-methyl	69	46	23		1
Difenconazole	48	42	4	2	1
Epoxiconazole	45	40	2	3	3
Glyphosate	5	5			
Iprodione	58	36	18	4	1
Malathion	65	53	9	3	2
Pirimicarb	43	41	1	1	22
Prochloraz	54	48	5	1	3
Spiroxamin	51	36	8	7	2
Trifloxystrobin	61	59	2		

Results - > 90% acceptable

	No. of reported results	Acceptable	Questionable	Unacceptable	False negatives
Azoxystrobin	64	57	7		0
Alpha-cypermethrir	43	40	3		8
Cypermethrin	29	21	5	3	31
Cypermethrin all	58	58			3
Bifentrin	64	59	5		1
Carbendazim	47	38	8	1	2
Chlormequat	26	24	2		
Chlorpyrifos-methyl	69	46	23		1
Difenconazole	48	42	4	2	1
Epoxiconazole	45	40	2	3	3
Glyphosate	5	5			
Iprodione	58	36	18	4	1
Malathion	65	53	9	3	2
Pirimicarb	43	41	1	1	22
Prochloraz	54	48	5	1	3
Spiroxamin	51	36	8	7	2
Trifloxystrobin	61	59	2		

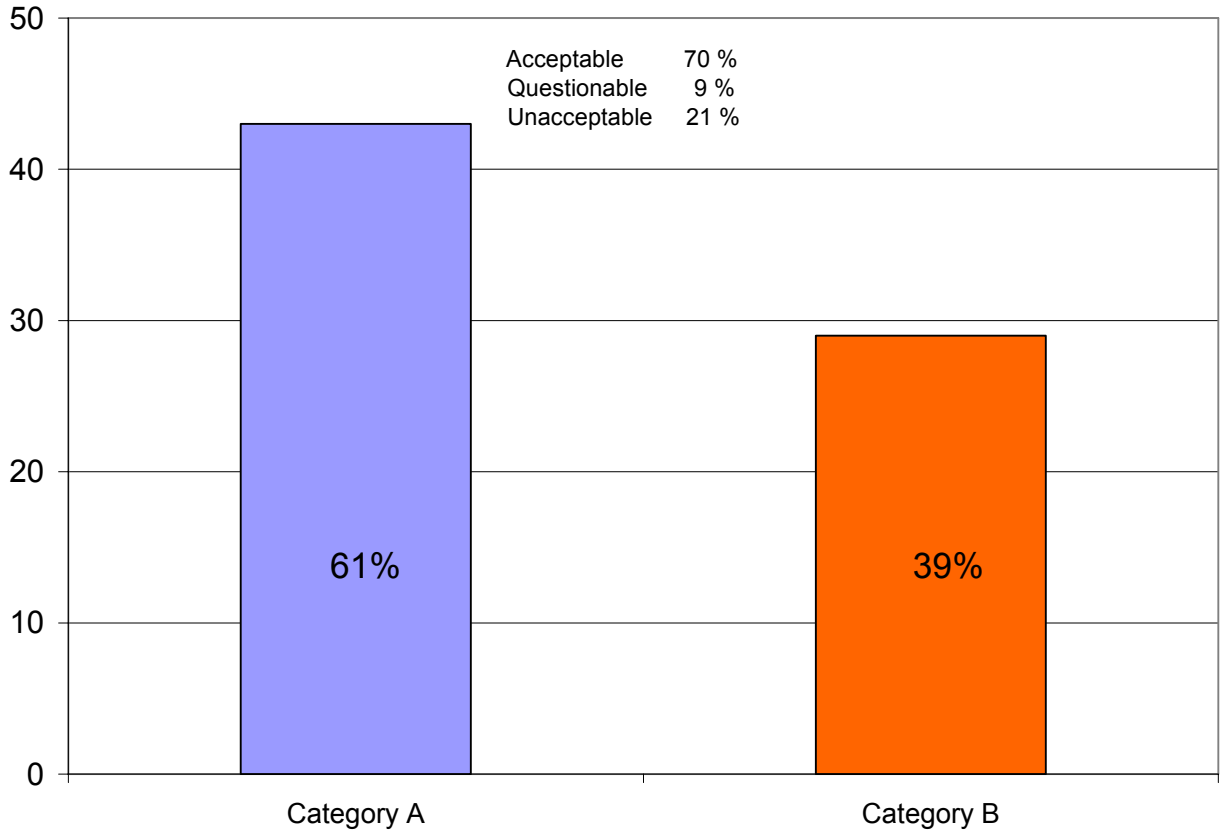
Results – 80-90% acceptable

	No. of reported results	Acceptable	Questionable	Unacceptable	False negatives
Azoxystrobin	64	57	7		0
Alpha-cypermethrir	43	40	3		8
Cypermethrin	29	21	5	3	31
Cypermethrin all	58	58			3
Bifentrin	64	59	5		1
Carbendazim	47	38	8	1	2
Chlormequat	26	24	2		
Chlorpyrifos-methyl	69	46	23		1
Difenconazole	48	42	4	2	1
Epoxiconazole	45	40	2	3	3
Glyphosate	5	5			
Iprodione	58	36	18	4	1
Malathion	65	53	9	3	2
Pirimicarb	43	41	1	1	22
Prochloraz	54	48	5	1	3
Spiroxamin	51	36	8	7	2
Trifloxystrobin	61	59	2		

Results - <80% acceptables

	No. of reported results	Acceptable	Questionable	Unacceptable	False negatives
Azoxystrobin	64	57	7		0
Alpha-cypermethrir	43	40	3		8
Cypermethrin	29	21	5	3	31
Cypermethrin all	58	58			3
Bifentrin	64	59	5		1
Carbendazim	47	38	8	1	2
Chlormequat	26	24	2		
Chlorpyrifos-methyl	69	46	23		1
Difenconazole	48	42	4	2	1
Epoxiconazole	45	40	2	3	3
Glyphosate	5	5			
Iprodione	58	36	18	4	1
Malathion	65	53	9	3	2
Pirimicarb	43	41	1	1	22
Prochloraz	54	48	5	1	3
Spiroxamin	51	36	8	7	2
Trifloxystrobin	61	59	2		

Catagory A and B



Weighted z-scores