

**EU proficiency test on Cereals –  
CRL for Cereals and Feeding stuff  
EU-PTC2  
(part 2)**

3th CRL/NRL workshop, Copenhagen 2008

## Results of the PTC2 (continued)

- The effect of adding water prior to extraction
- Extraction method and average z-scores
- Will look at possible effect of different:
  - Clean up method
  - Calibrations
  - Accreditation status
- Summary

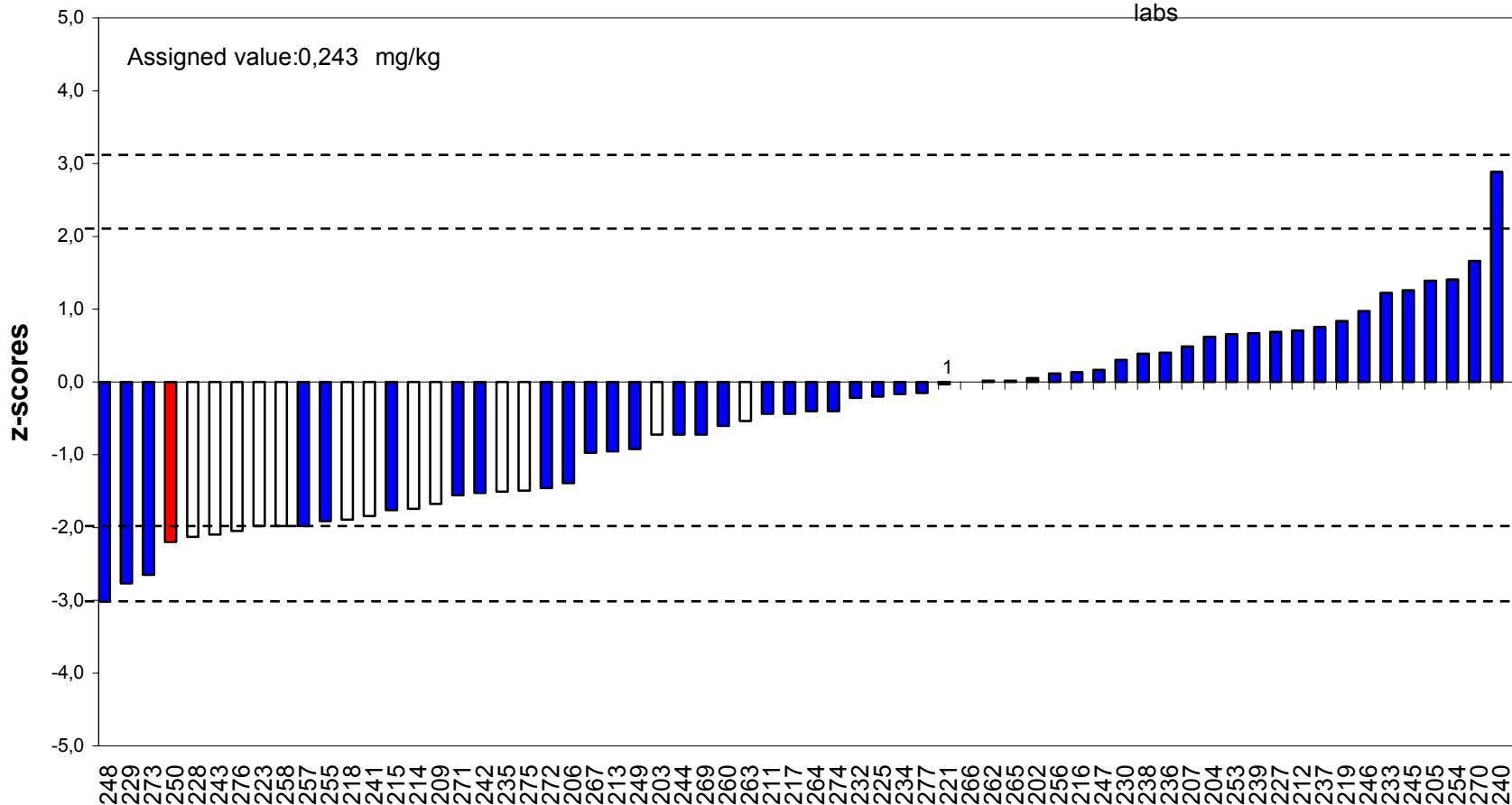
# Water addition

Pesticide	WATER ADDITION	NO WATER ADDED
Azoxystrobin	49	14
Bifenthrin	43	19
Alpha-cypermethrin	27	13
Cypermethrin	21	5
Carbendazim	36	9
Chlormequat	22	2
Chlorpyrifos-methyl	48	16
Difenconazole	41	6
Epoxiconazole	40	3
Iprodione	43	13
Malathion	39	13
Pirimicarb	45	2
Prochloraz	43	10
Spiroxamin	44	5
Trifloxystrobin	48	12

- or 1: No water added
- or 2: Water added
- or 3: not specified

# Azoxystrobin

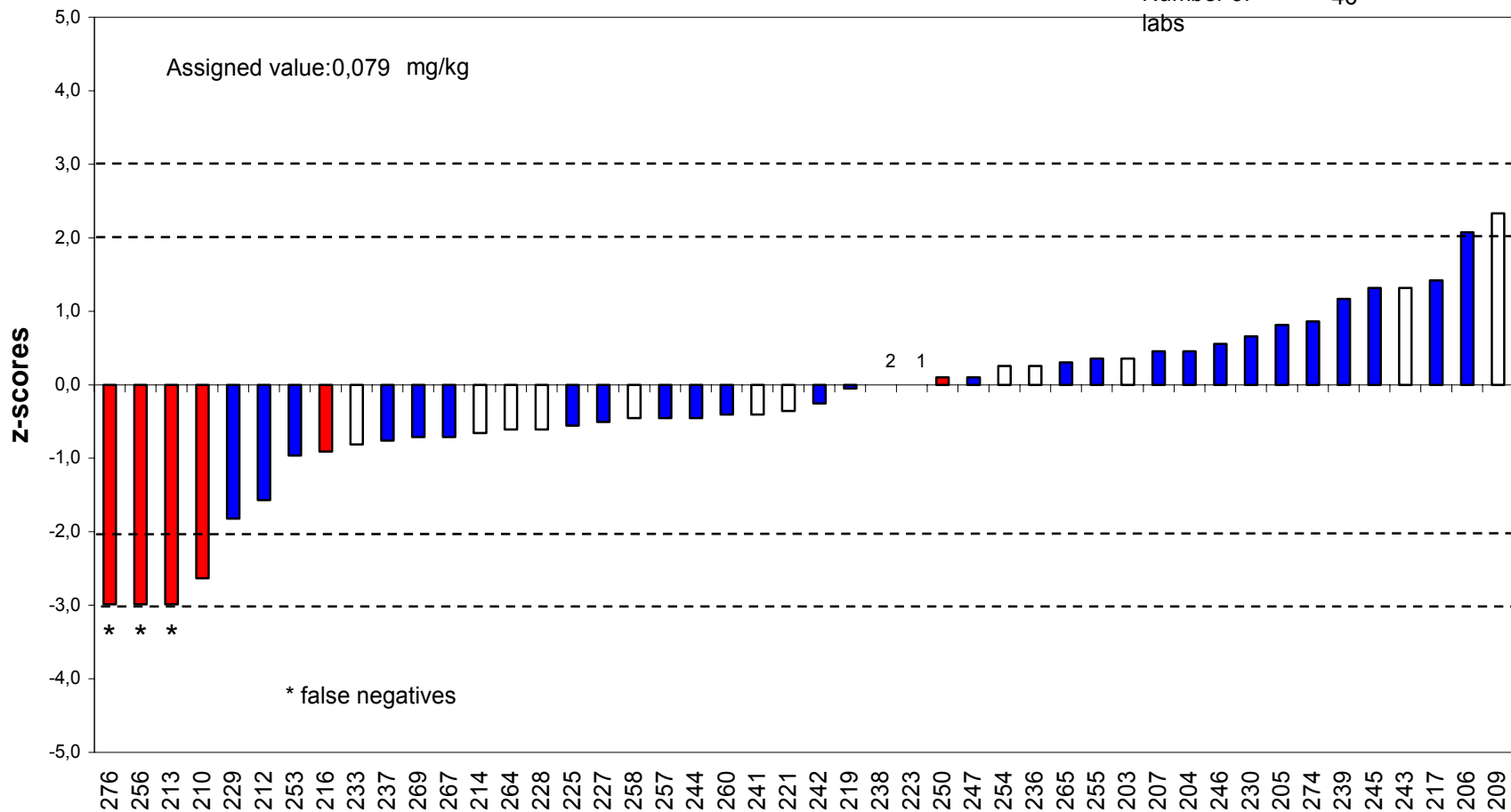
Acceptable 91%  
 Questionable 9%  
 Unacceptable 0%  
 Number of labs 64



- or 1: No water added
- or 2: Water added
- or 3: not specified

## Alpha-cypermethrin

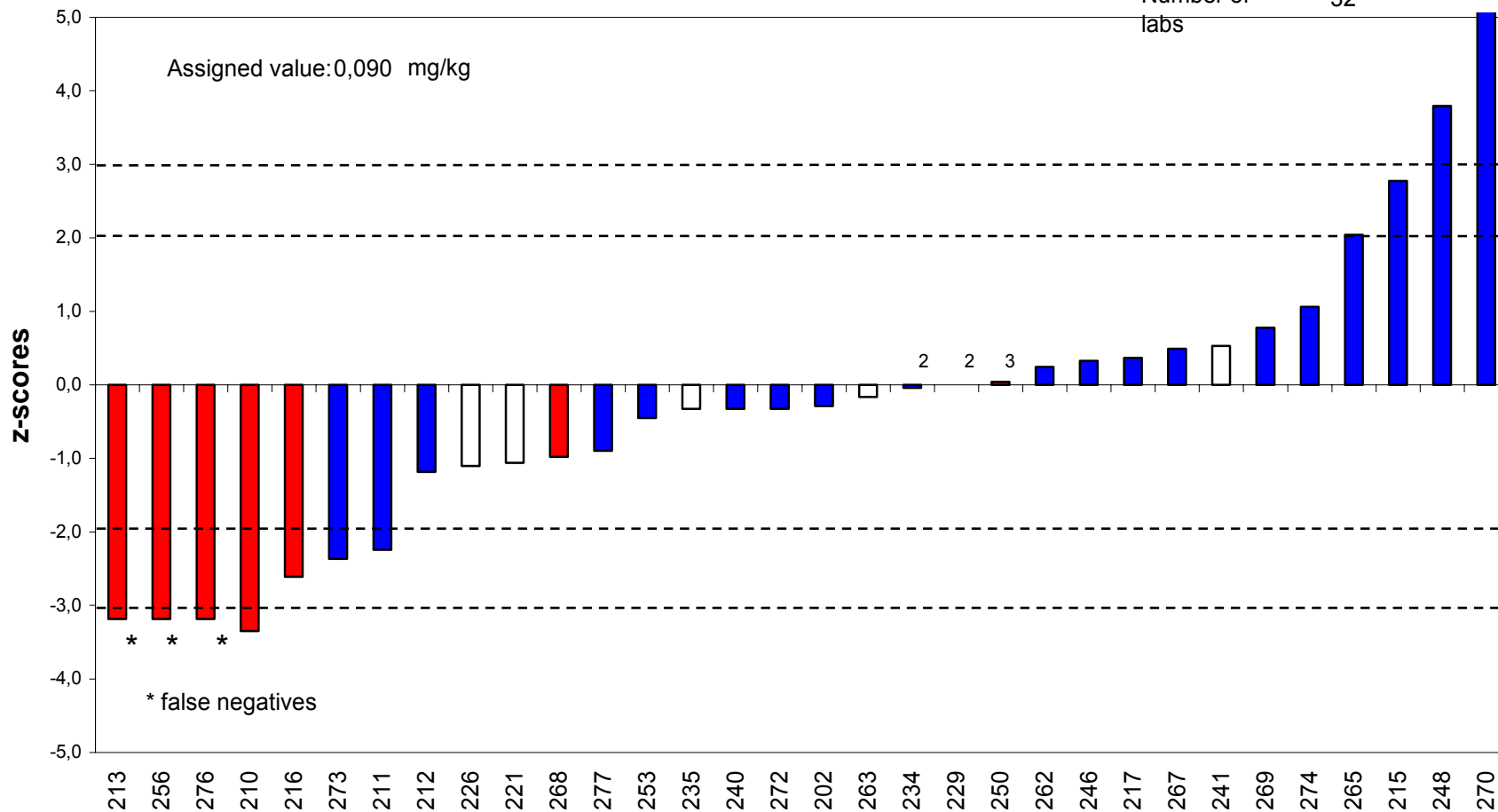
Acceptable 87%  
 Questionable 7%  
 Unacceptable 7%  
 Number of labs 46



- or 1: No water added
- or 2: Water added
- or 3: not specified

## Cypermethrin

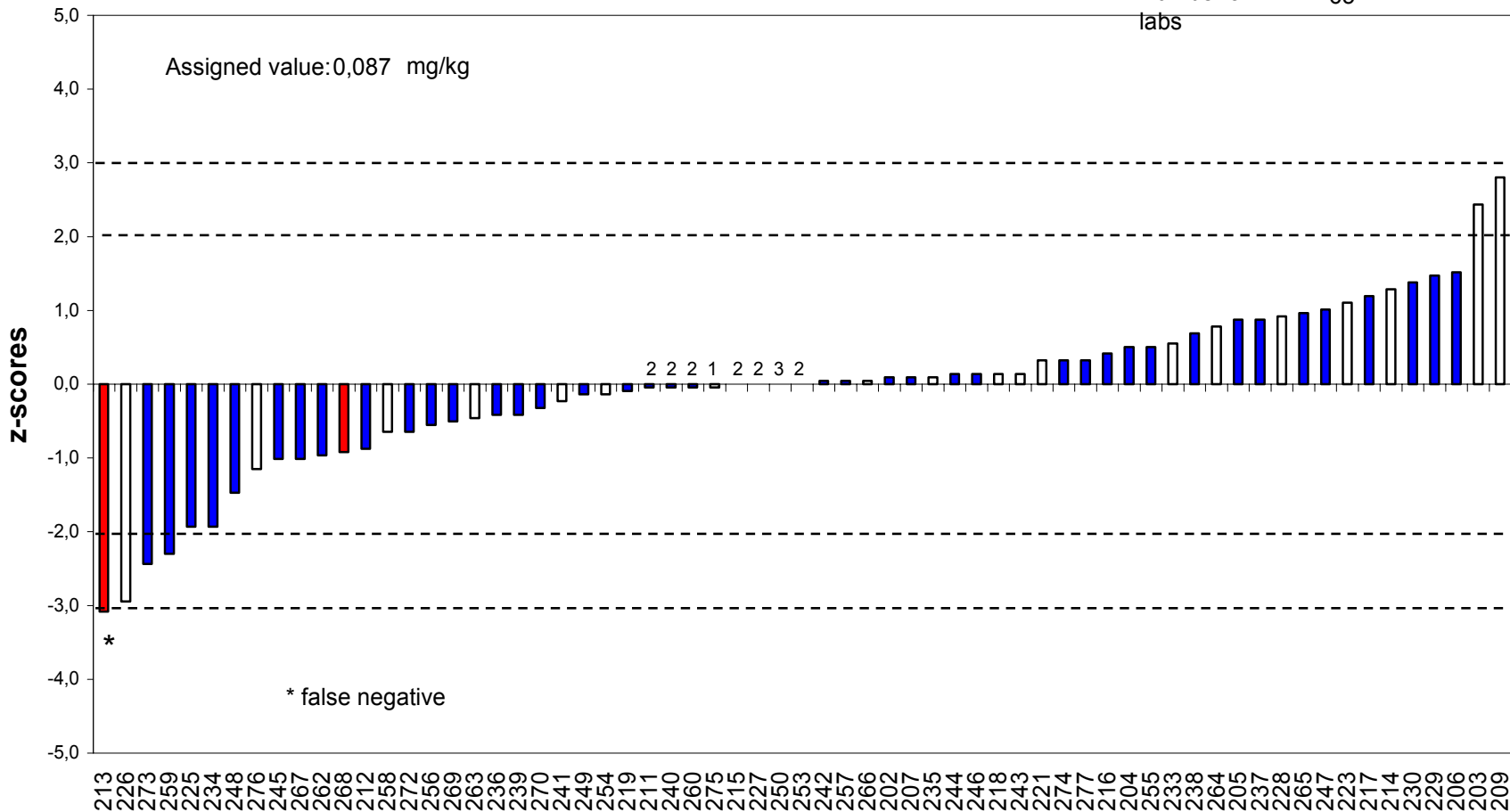
Acceptable 66%  
 Questionable 16%  
 Unacceptable 19%  
 Number of labs 32



- or 1: No water added
- or 2: Water added
- or 3: not specified

# Bifenthrin

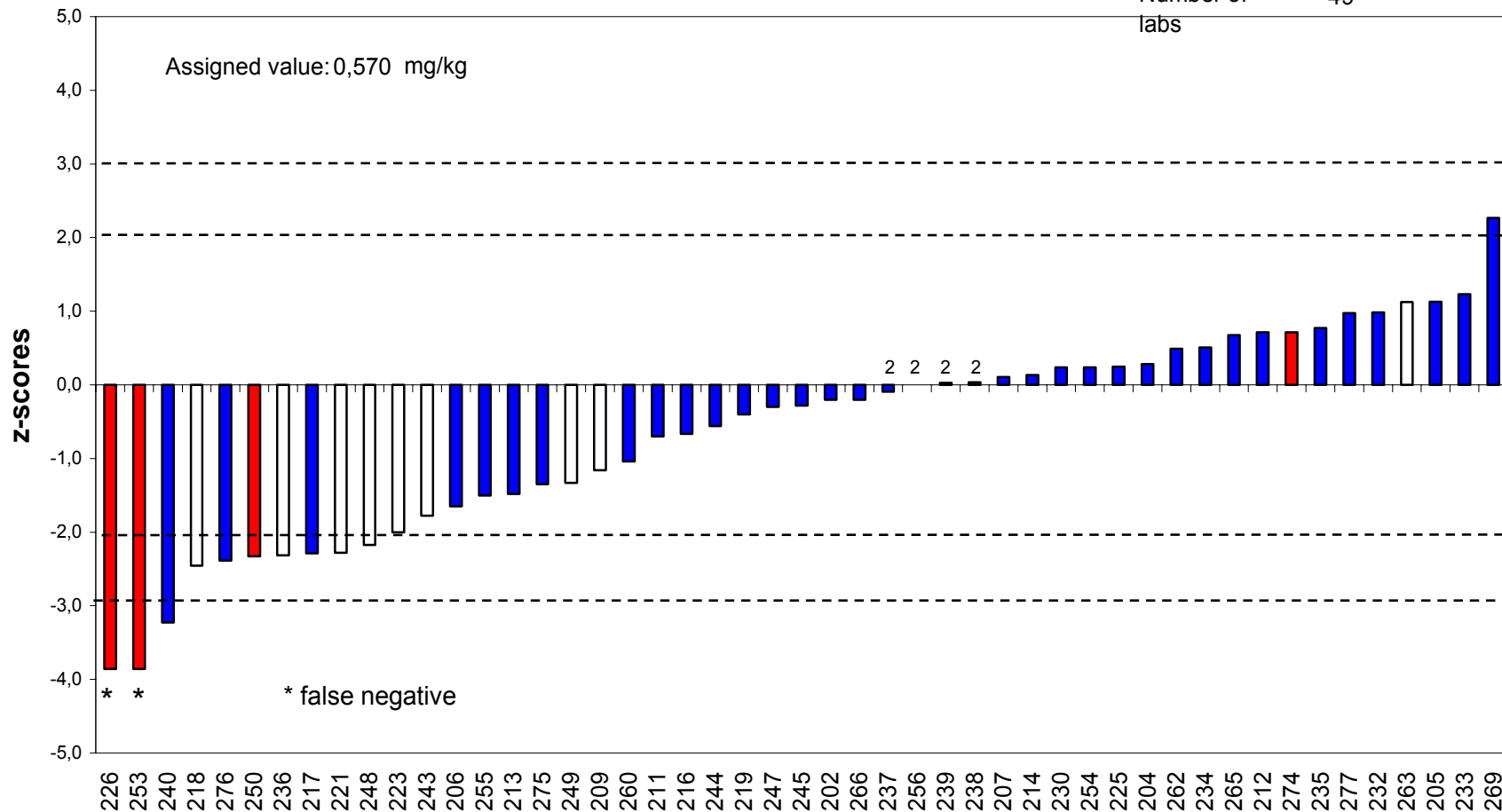
Acceptable 91%  
 Questionable 8%  
 Unacceptable 2%  
 Number of labs 65



- or 1: No water added
- or 2: Water added
- or 3: not specified

## Carbendazim

Acceptable 78%  
 Questionable 16%  
 Unacceptable 6%  
 Number of 49  
 labs

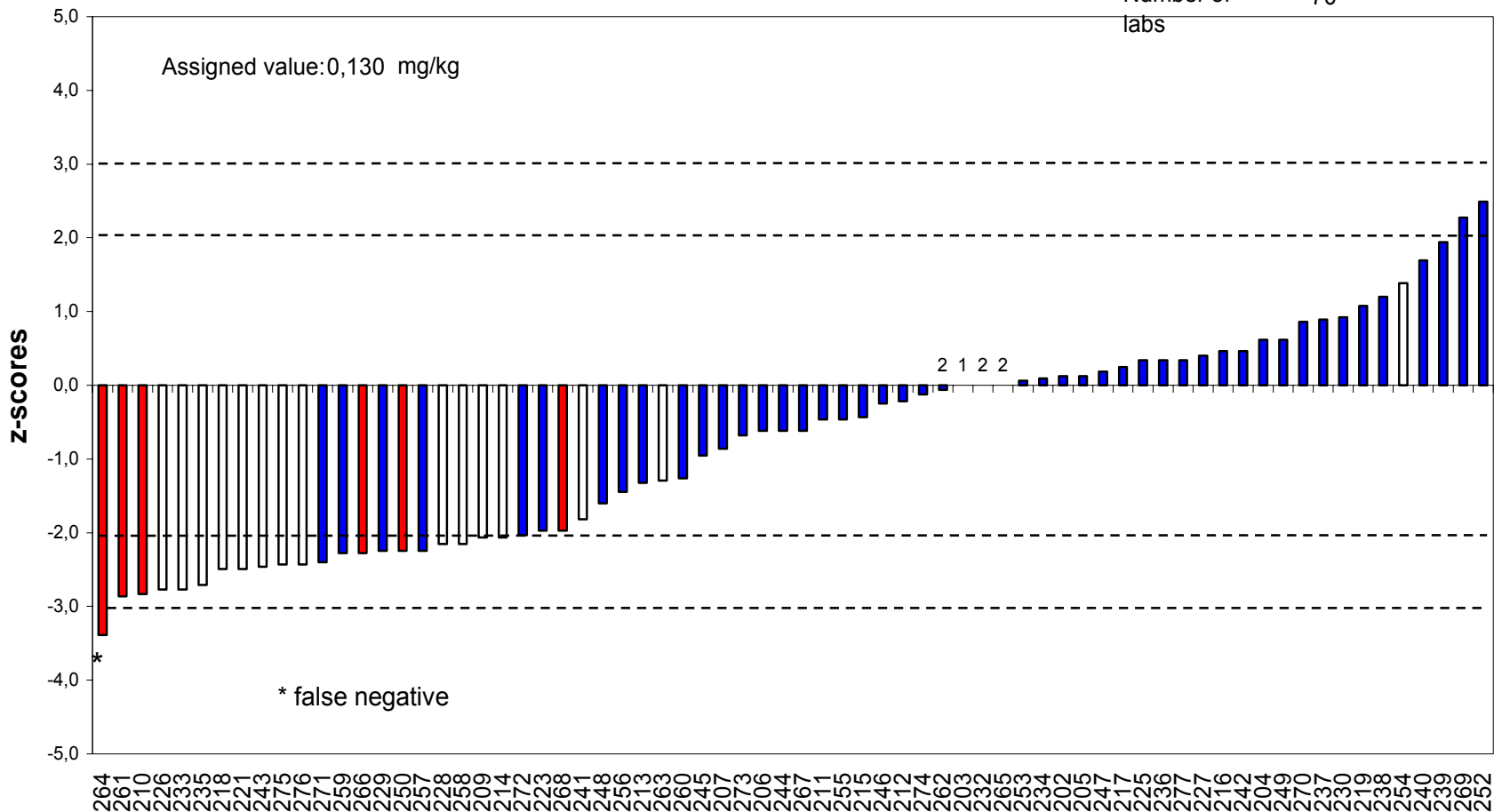




- or 1: No water added
- or 2: Water added
- or 3: not specified

# Chlorpyrifos-methyl

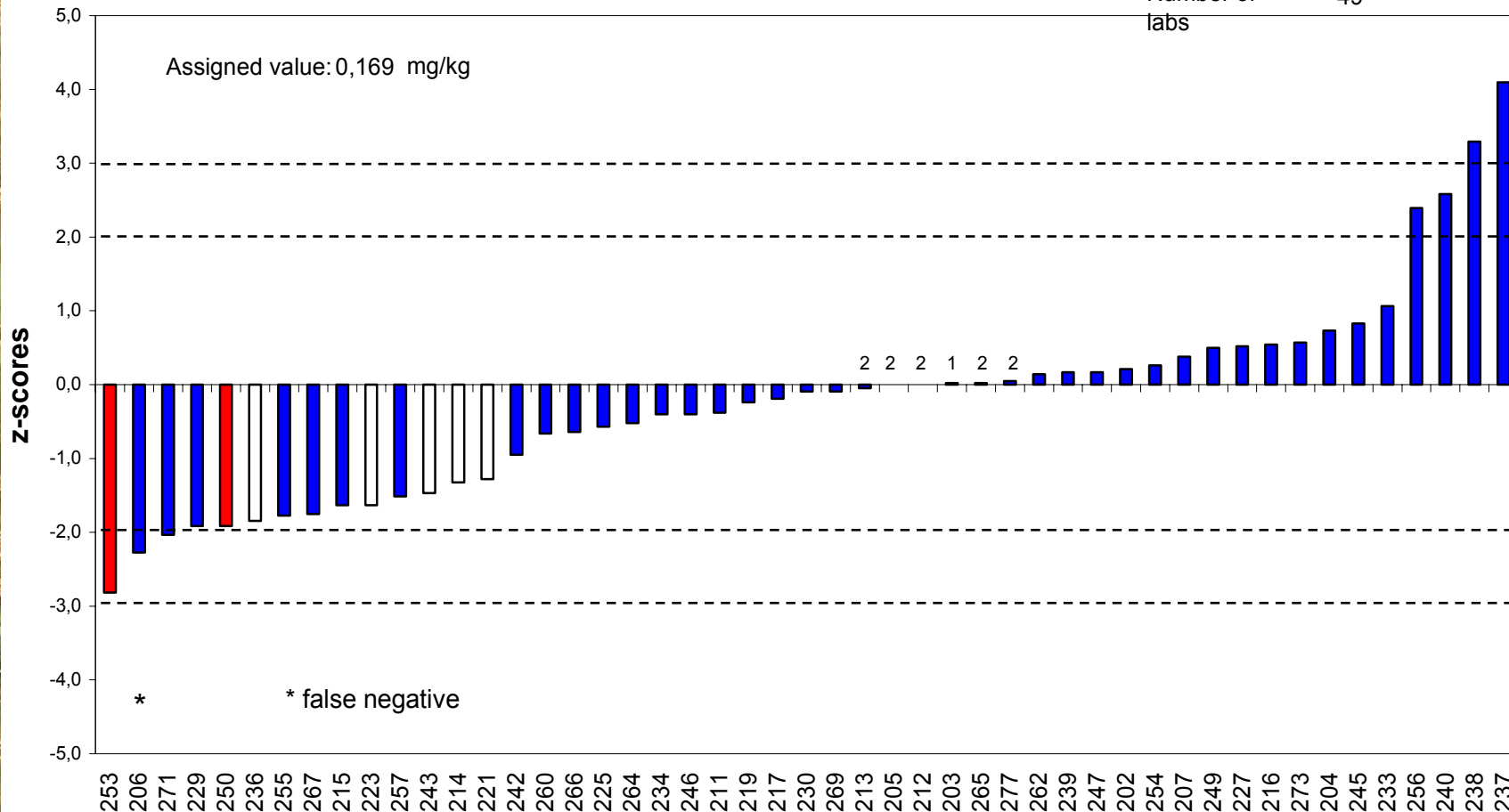
Acceptable 66%  
 Questionable 33%  
 Unacceptable 1%  
 Number of labs 70



# Difenconazole

- or 1: No water added
- or 2: Water added
- or 3: not specified

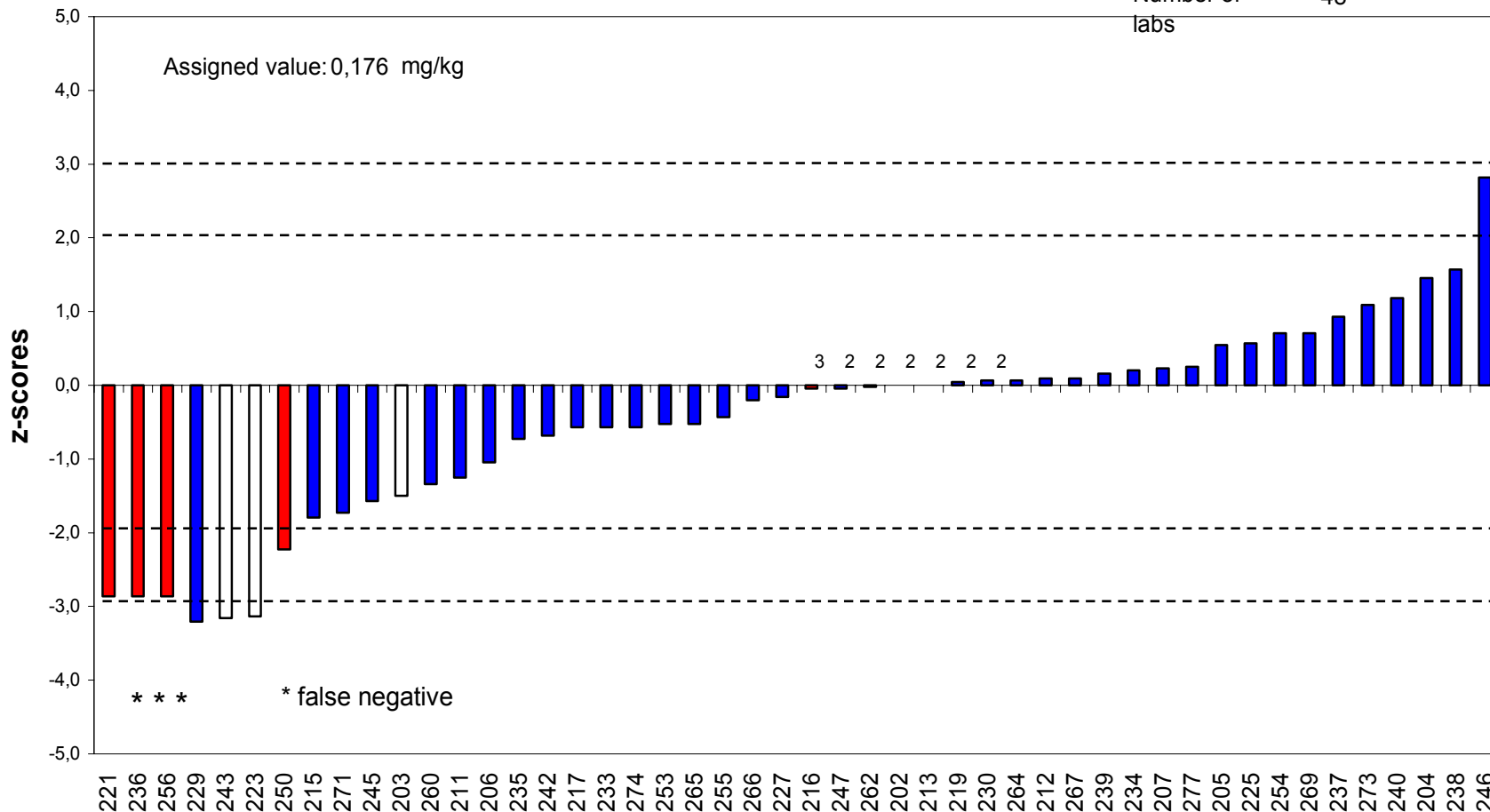
Acceptable 86%  
 Questionable 10%  
 Unacceptable 4%  
 Number of labs 49



- or 1: No water added
- or 2: Water added
- or 3: not specified

# Epoxiconazole

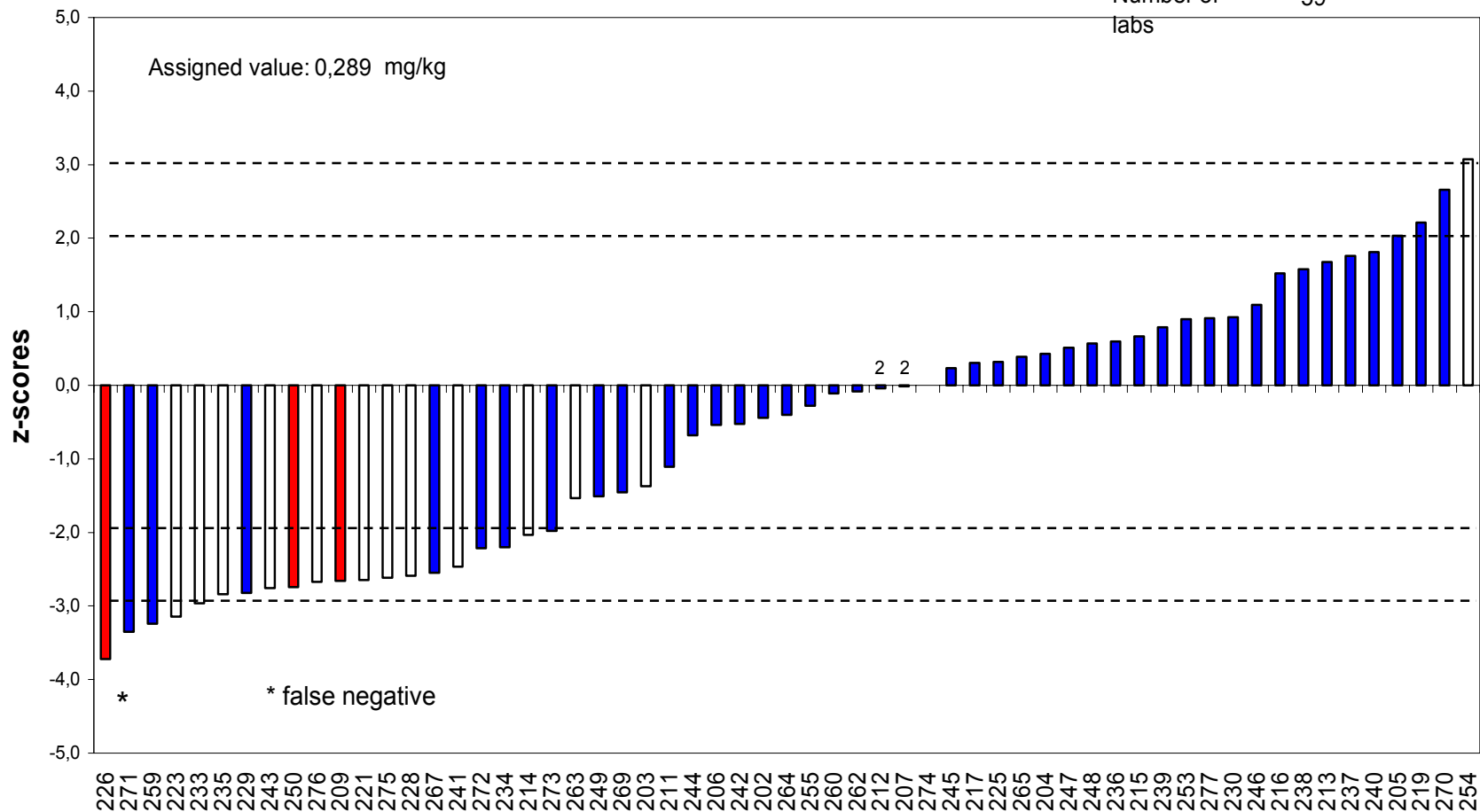
Acceptable 83%  
 Questionable 4%  
 Unacceptable 6%  
 Number of labs 48



- or 1: No water added
- or 2: Water added
- or 3: not specified

## Iprodione

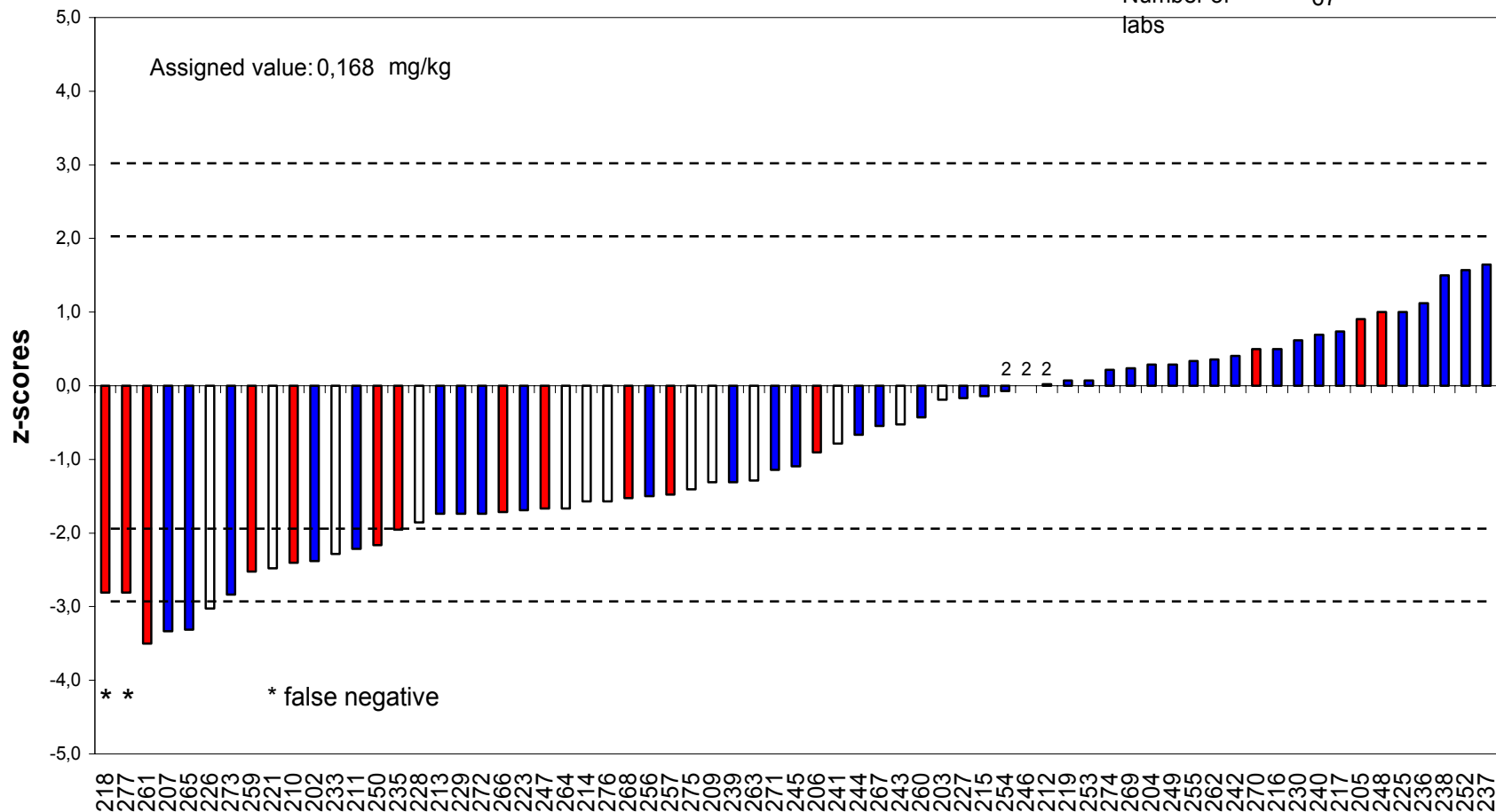
Acceptable 61%  
 Questionable 31%  
 Unacceptable 8%  
 Number of 59  
 labs



- or 1: No water added
- or 2: Water added
- or 3: not specified

# Malation

Acceptable 79%  
 Questionable 13%  
 Unacceptable 4%  
 Number of labs 67

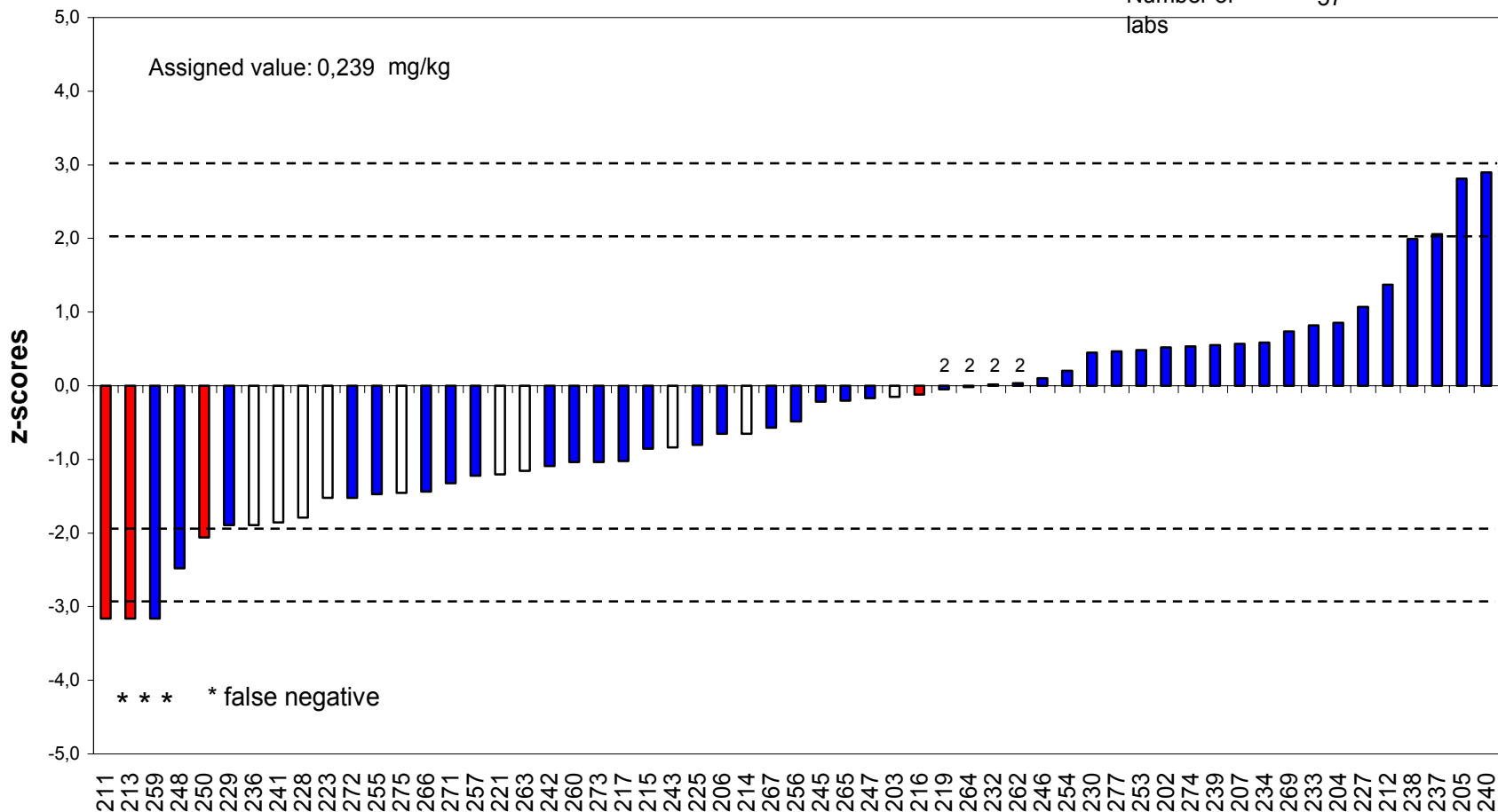




# Procloraz

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

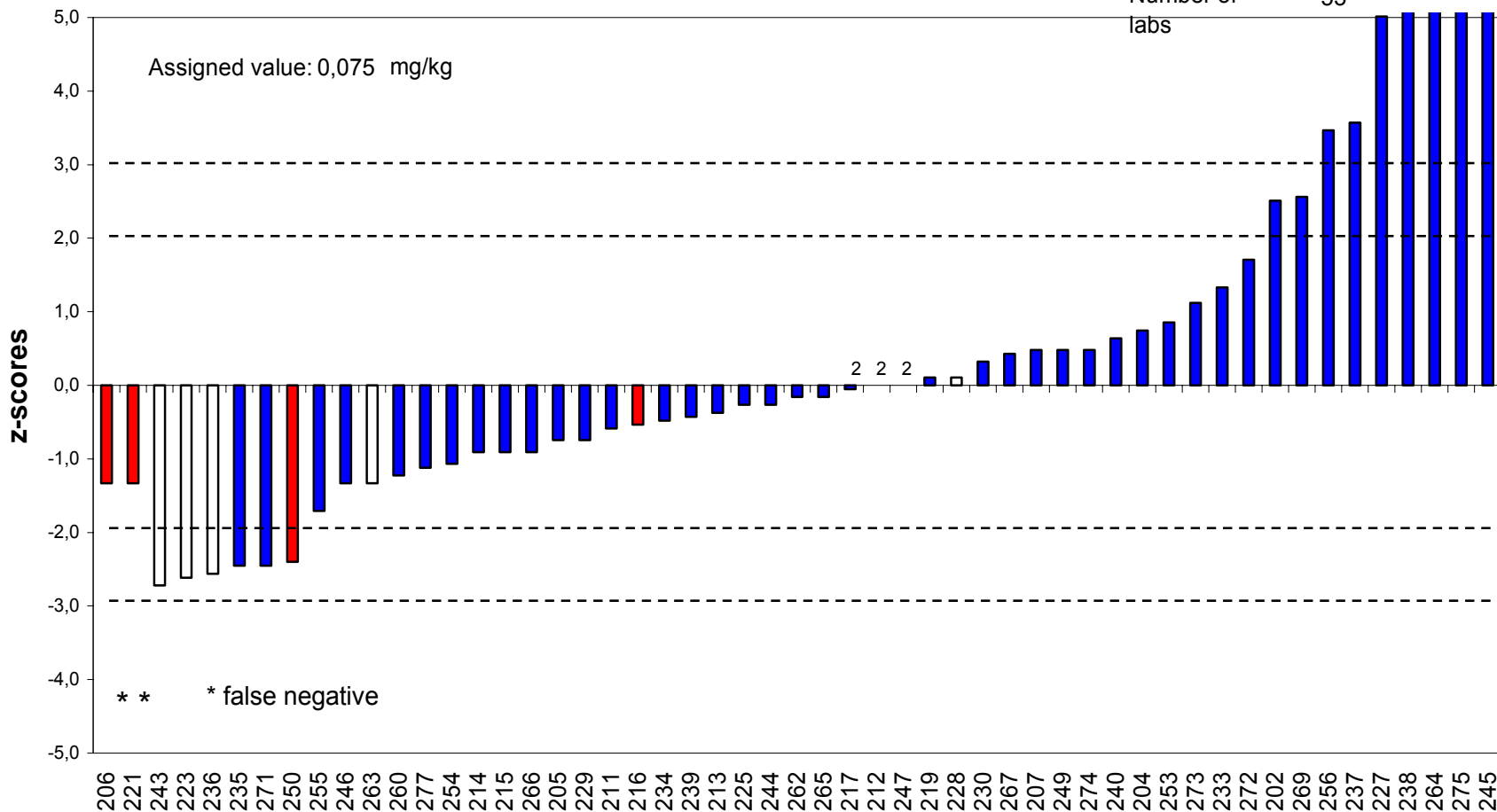
□ or 1: No water added  
 ■ or 2: Water added  
 ■ or 3: not specified



# Spiroxamin

- or 1: No water added
- or 2: Water added
- or 3: not specified

Acceptable 68%  
 Questionable 15%  
 Unacceptable 13%  
 Number of labs 53

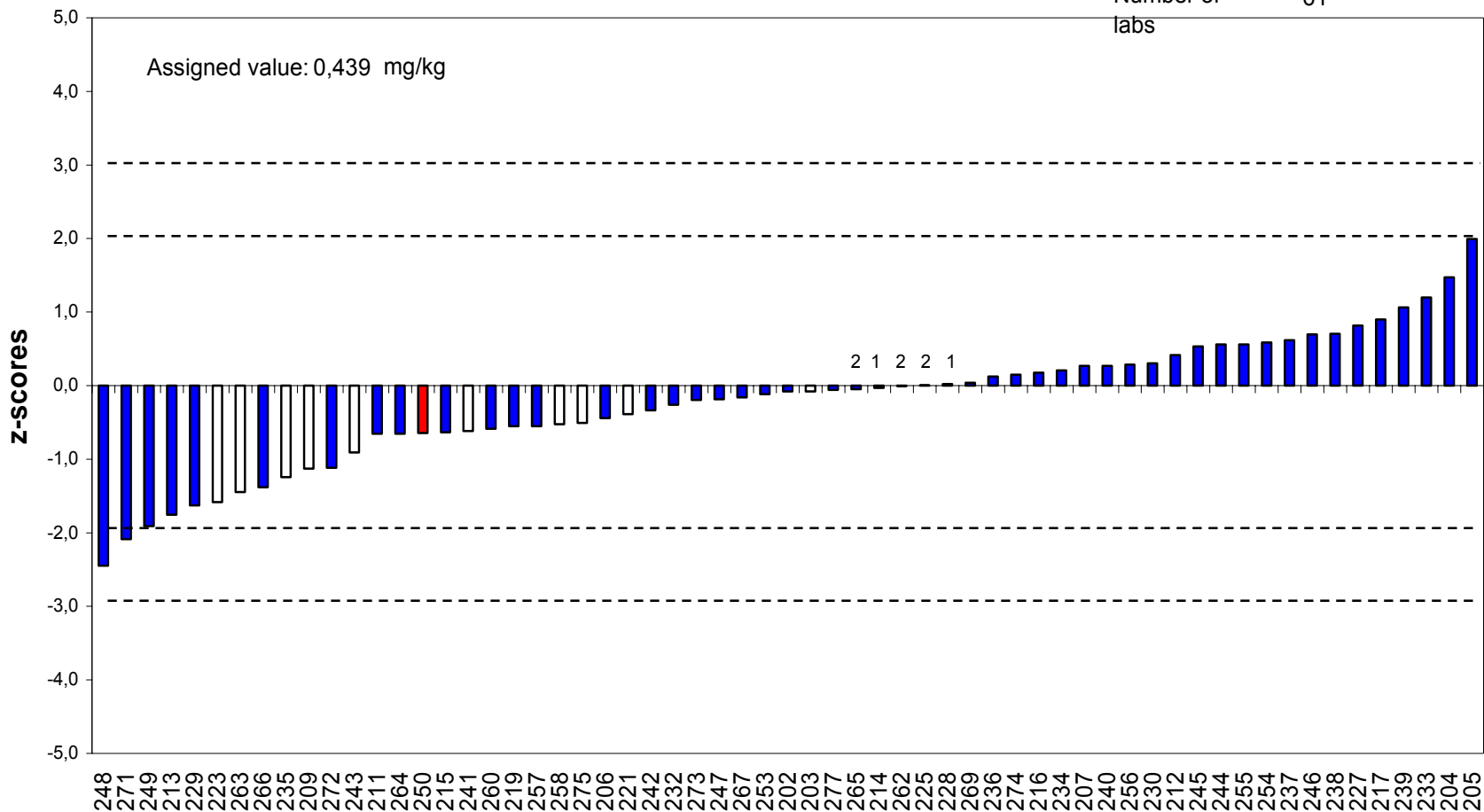




- or 1: No water added
- or 2: Water added
- or 3: not specified

## Trifloxystrobin

Acceptable 97%  
 Questionable 3%  
 Unacceptable 0%  
 Number of 61  
 labs



## Water addition

<b>Increased extraction efficiency by adding water</b>	<b>No clear effect on extraction efficiency by addition water</b>
Azoxystrobin	Alpha-cypermethrin
Chlomequat	Cypermethrin
Chlorpyrifos-methyl	Bifentrin
Difenconazole	
Epoxiconazole	
Glyphosate	
Iprodione	
Malathion	
(Pirimicarb)	
Prochloraz	
Spiroxamin	
Trifloxystrobin	

# SANCO/2007/3131

(Method validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed)

- The following has been included in the SANCO document:

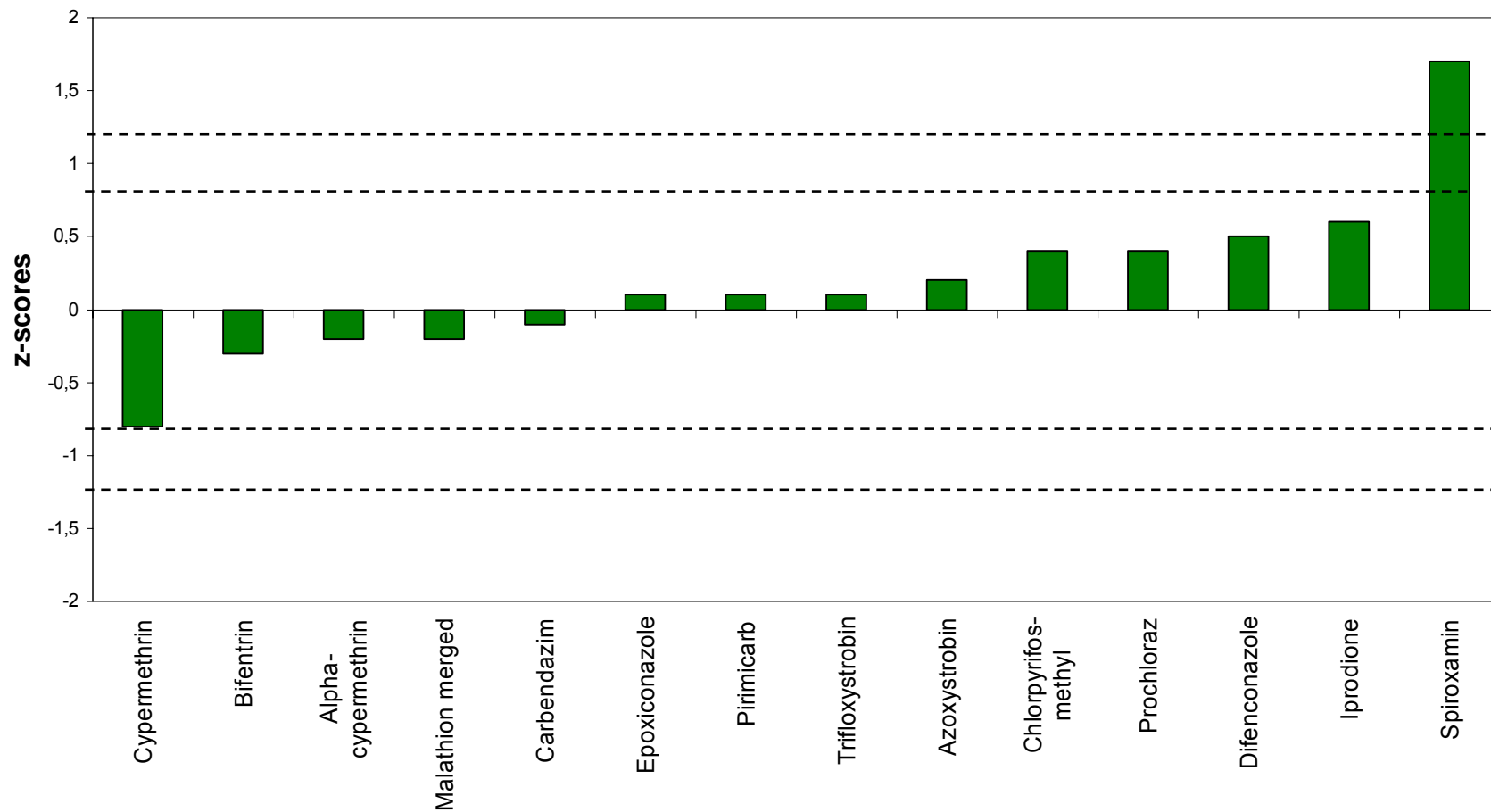
*”To improve the extraction efficiency of low moisture containing commodities (cereals, dried fruits), it is recommended to add water to the samples before extraction is carried out”*

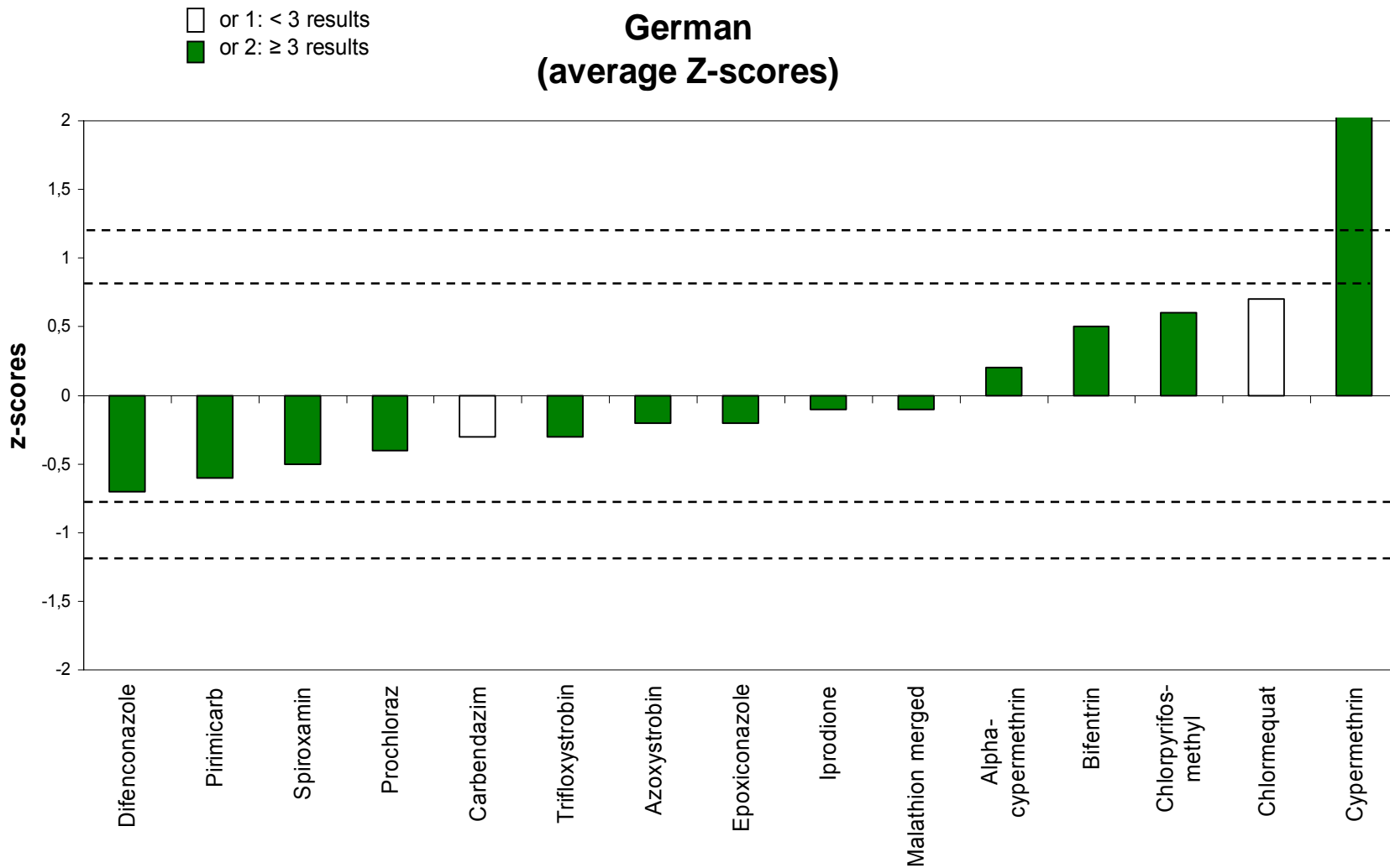
# Extraction method

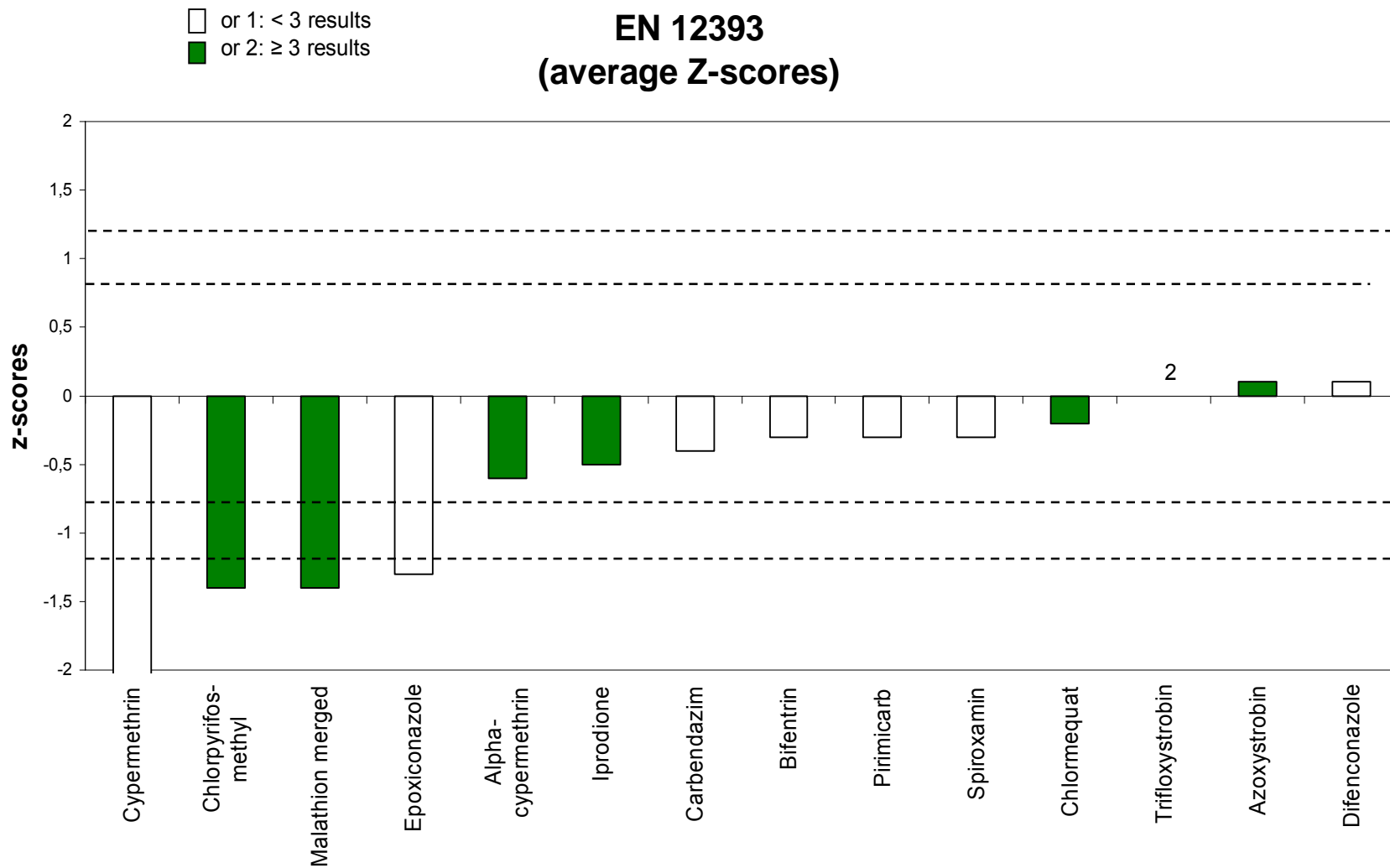
Pesticide	QuEChERS 1)	Dutch 2)	EN 12393	Luke	German 3)	Italian 4)	Other 5)	Total
Azoxystrobin	13	2	4	4	7	1	33	64
Bifenthrin	11	3	5	5	6	1	33	64
Alpha-cypermethrin	8	3	3	3	4	0	22	43
Cypermethrin	6	1	2	2	4	1	13	29
Carbendazim	12	0	2	1	2	0	30	47
Chlormequat			7		2		17	26
Chlorpyrifos-methyl	14	3	7	5	6	1	33	69
Difenconazole	13	1	2	2	6		24	48
Epoxiconazole	13	1	1	1	6		23	45
Iprodione	10	3	5	1	7	1	31	58
Malathion	13	1	6	2	6	1	36	65
Pirimicarb	13	1	2		8	1	19	44
Prochloraz	15	2		2	5	1	29	54
Spiroxamin	16		1	1	7	1	25	51
Trifloxystrobin	14	2	3	3	6	1	32	61

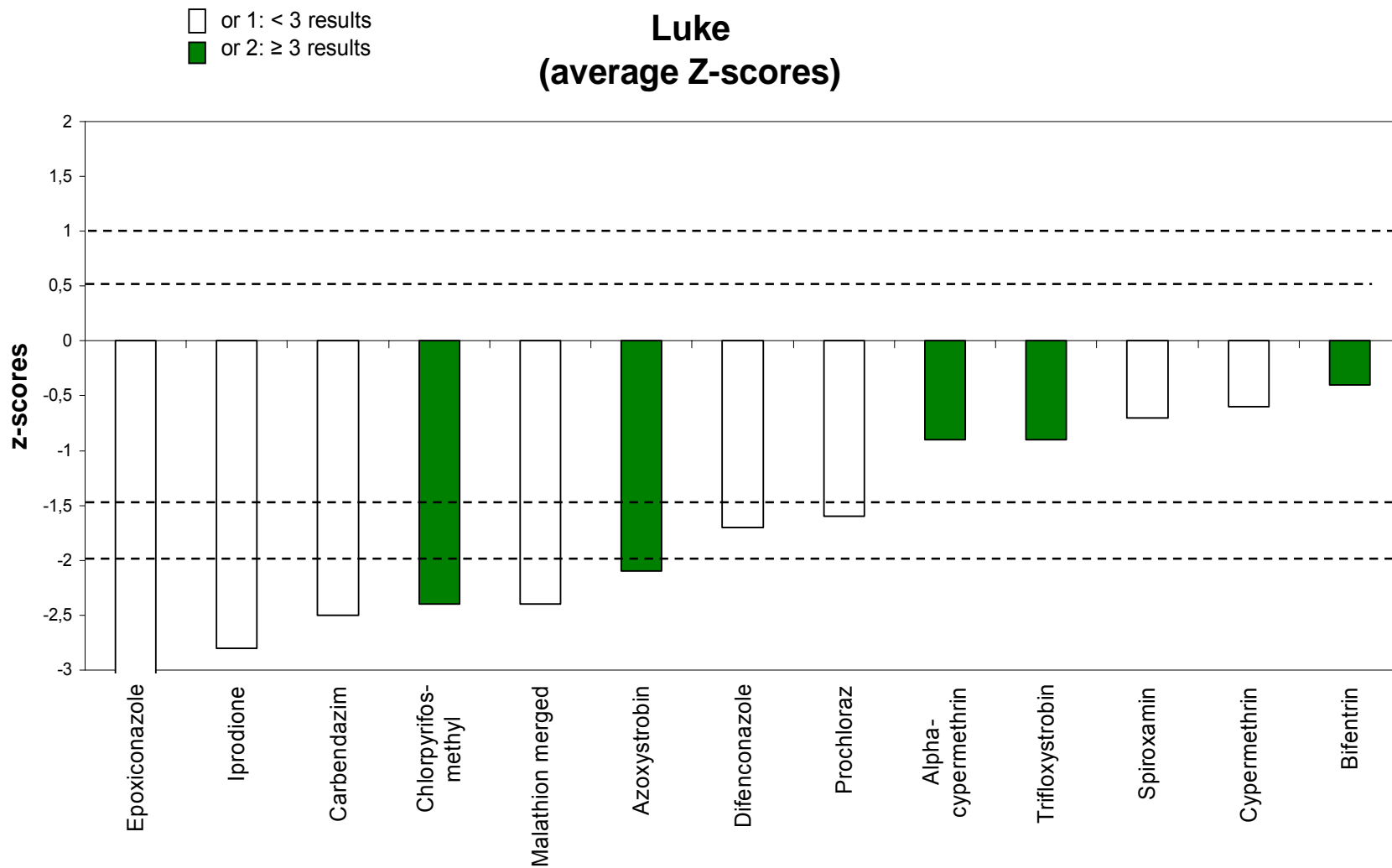
□ or 1: < 3 results  
■ or 2: ≥ 3 results

## QuEChERS (average Z-scores)











## Performance in relation to choice of method

- For some compound/method combination only few results are available so not conclusive
- However, the results of this PT indicate that the methods:
  - QuEChERS:
    - performs well for the compounds of this PT
  - German:
    - also performs well
  - EN 12393:
    - performs well but generally gives Z-scores below zero.
  - Luke:
    - results in relatively large Z-scores below zero (few results).

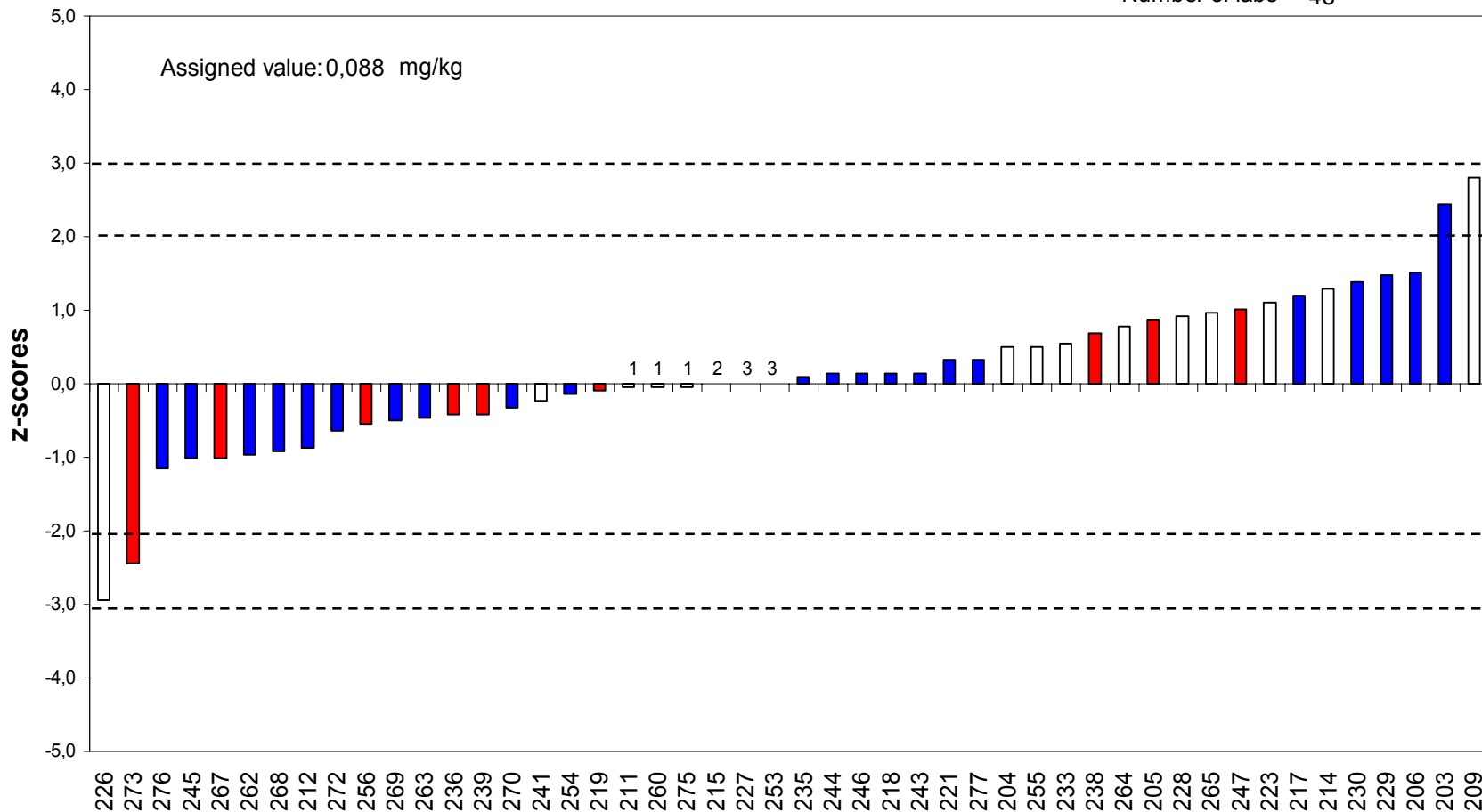
# Clean up

Pesticide	GPC	DSPE	SPE	None	Freezing out	liq./liq part.	Other
Azoxystrobin	19	11	4	15	5	2	3
Bifenthrin	23	11	4	6	3	2	3
Alpha-cypermethrin	14	9		11	2	2	3
Cypermethrin	13	4	3	5	1	2	
Carbendazim	6	9	4	11	4	6	1
Chlormequat			2	18		1	1
Chlorpyrifos-methyl	26	13	4	12	3	4	3
Difenconazole	11	12	3	11	4	1	2
Epoxiconazole	11	13	2	8	3	2	2
Iprodione	23	10	4	11	3	2	1
Malathion	19	11	2	13	4	1	1
Pirimicarb	13	11	3	6	5	2	2
Prochloraz	12	12	2	15	5	3	2
Spiroxamin	8	13	1	13	7	2	1
Trifloxystrobin	16	13	4	11	4	2	3

- or 1: No clean up
- or 2: GPC
- or 3: DSPE

## Bifenthrin Clean up

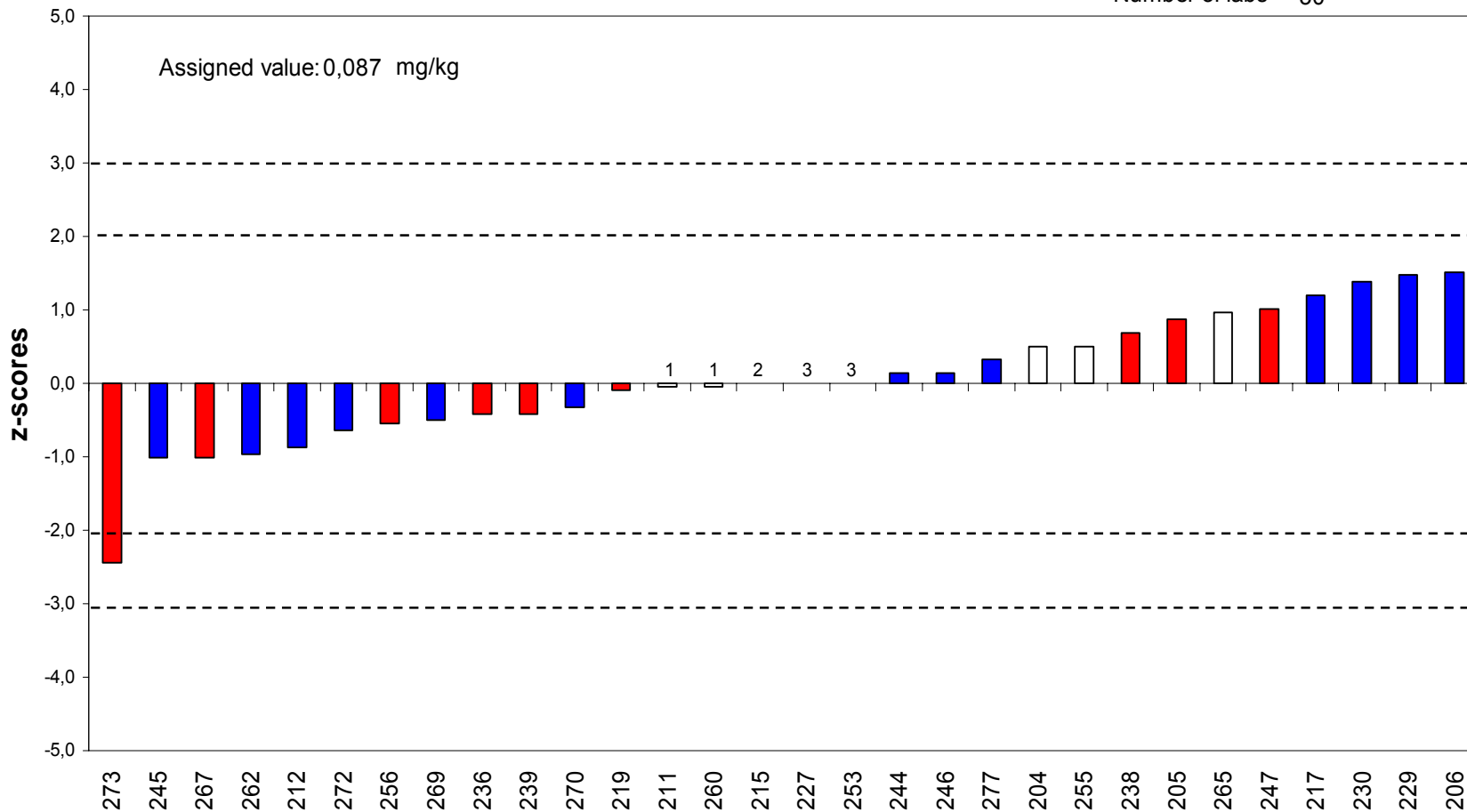
Acceptable 92%  
Questionable 8%  
Unacceptable 2%  
Number of labs 48



- or 1: No clean up
- or 2: GPC
- or 3: DSPE

## Bifenthrin Clean up

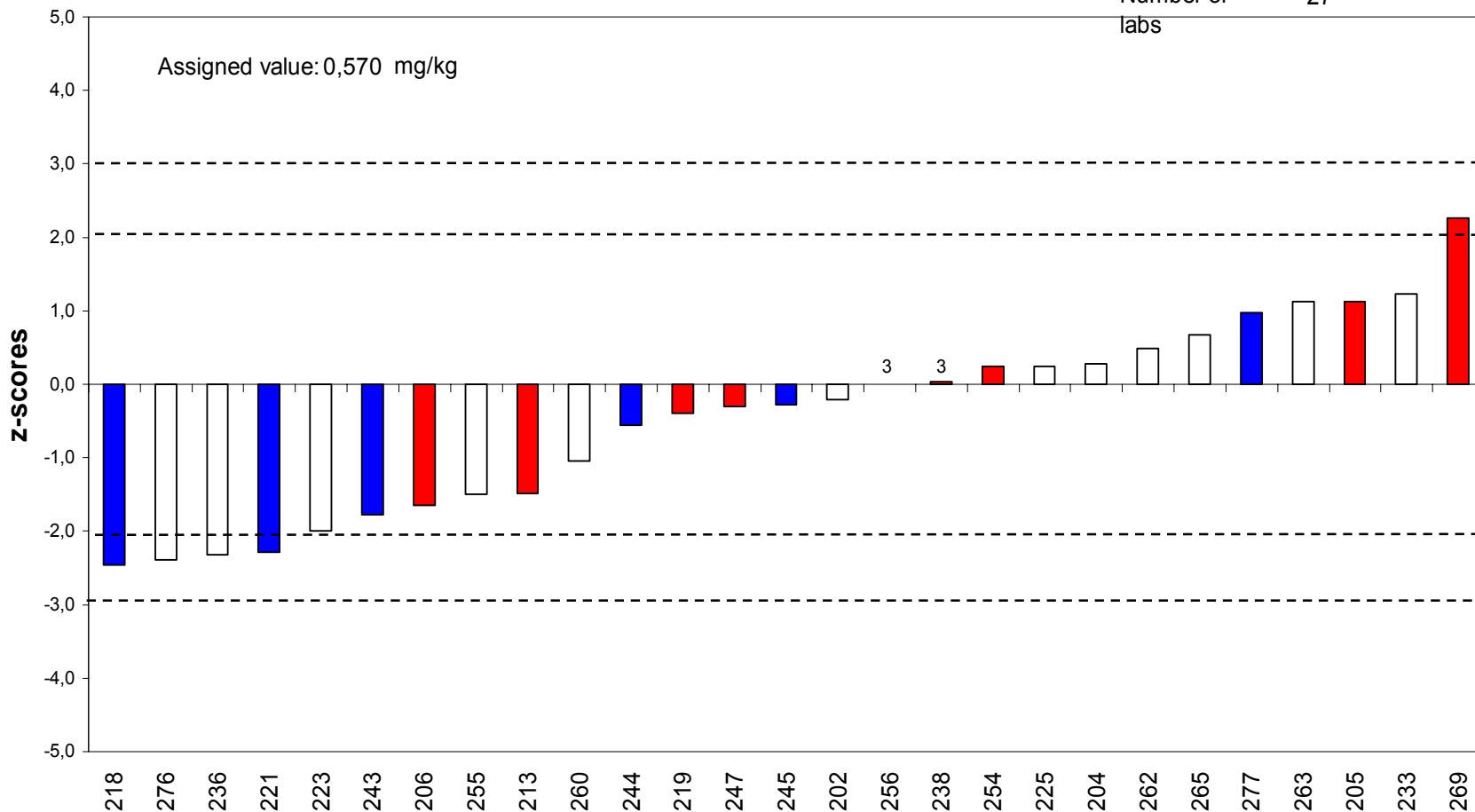
Acceptable 97%  
Questionable 7%  
Unacceptable 3%  
Number of labs 30

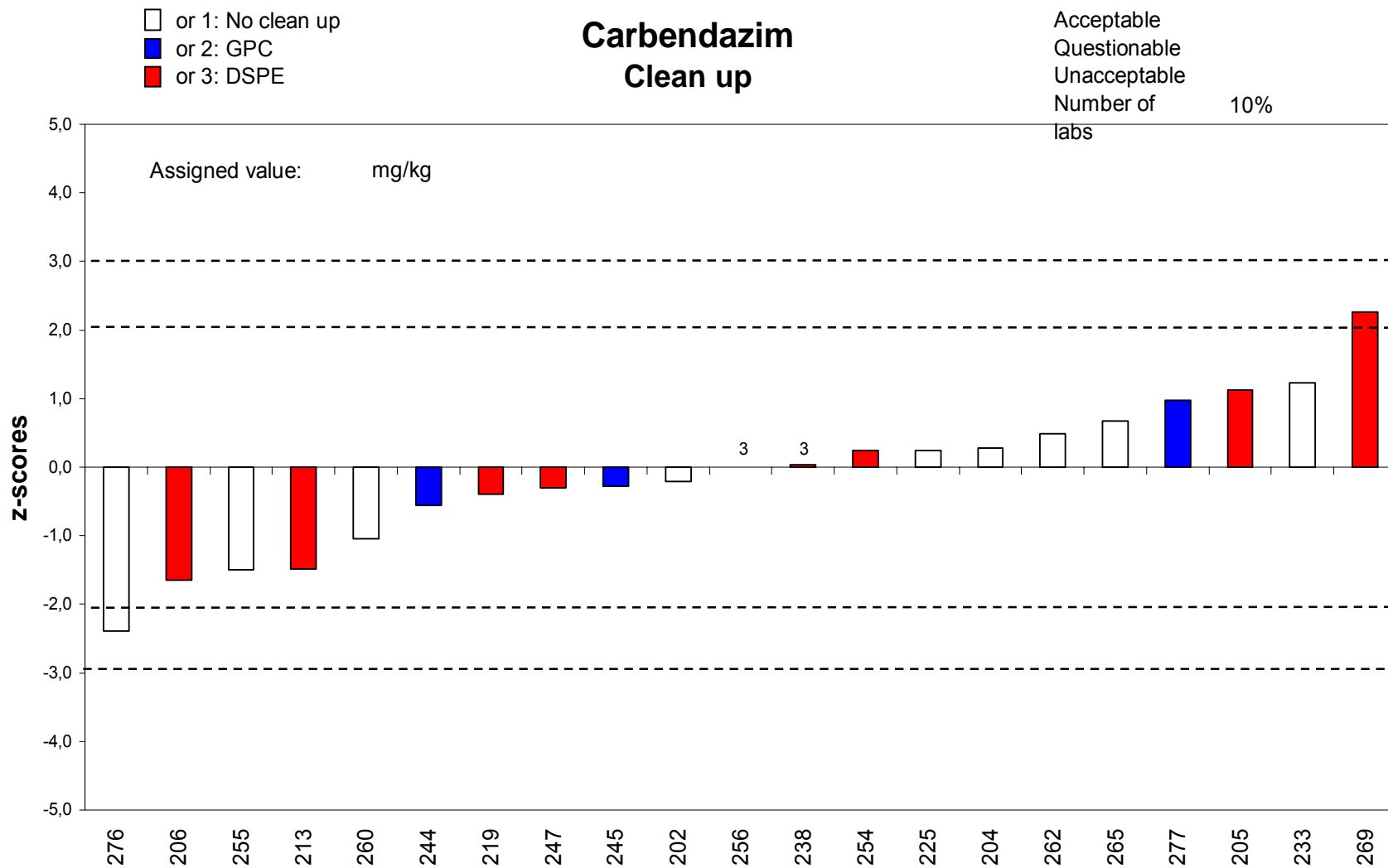


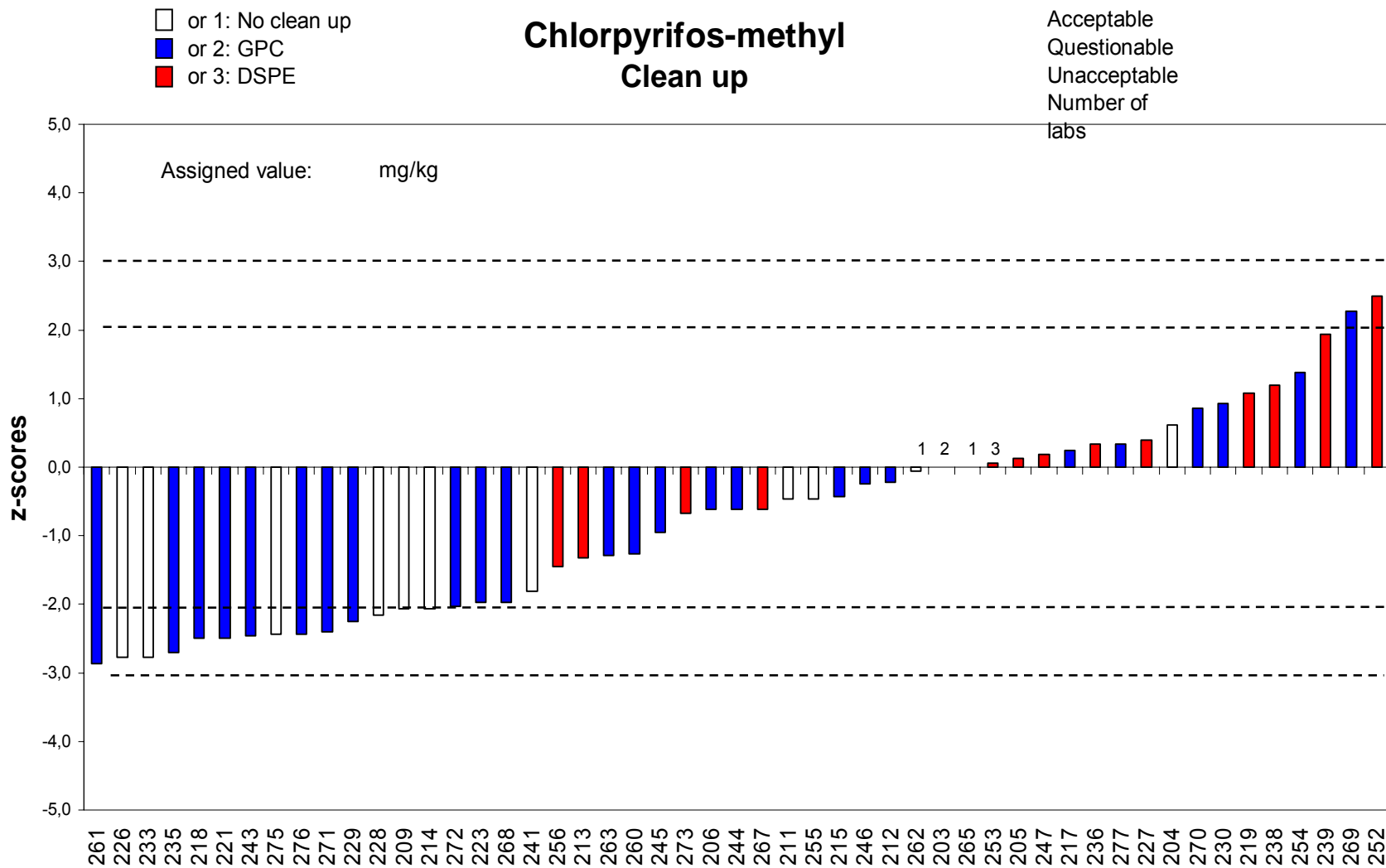
- or 1: No clean up
- or 2: GPC
- or 3: DSPE

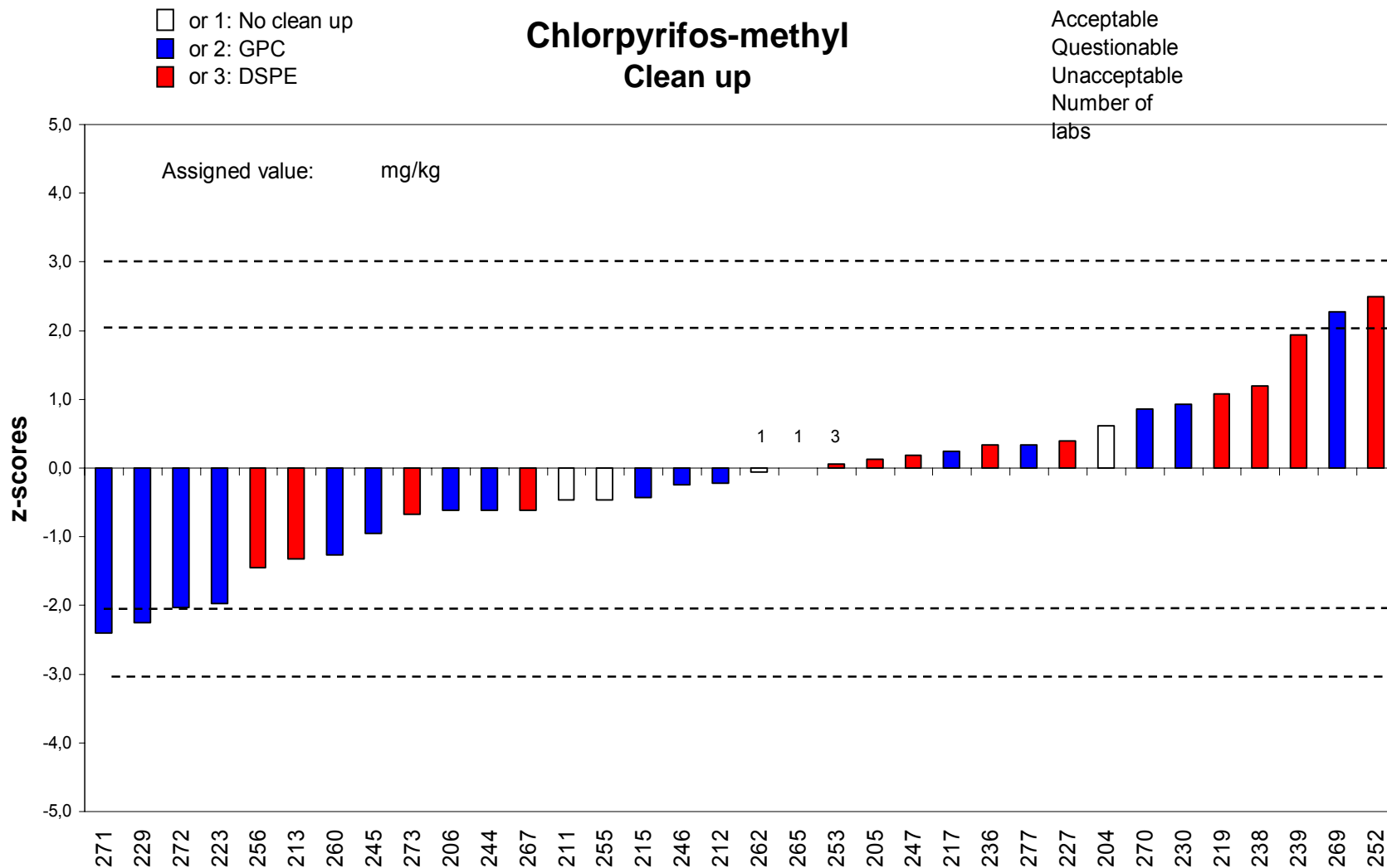
## Carbendazim Clean up

Acceptable 81%  
Questionable 19%  
Unacceptable 4%  
Number of  
labs 27











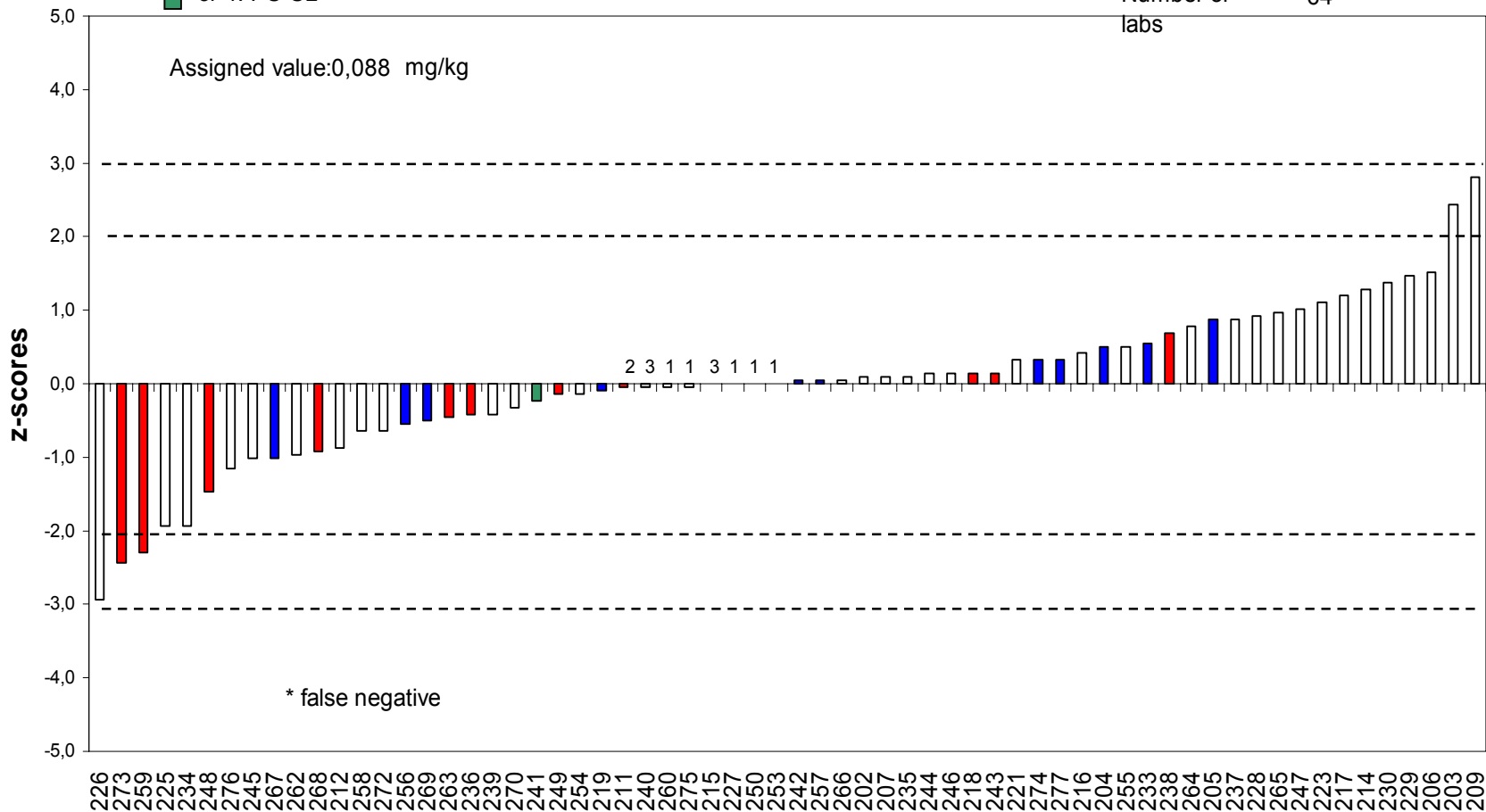
# Calibration

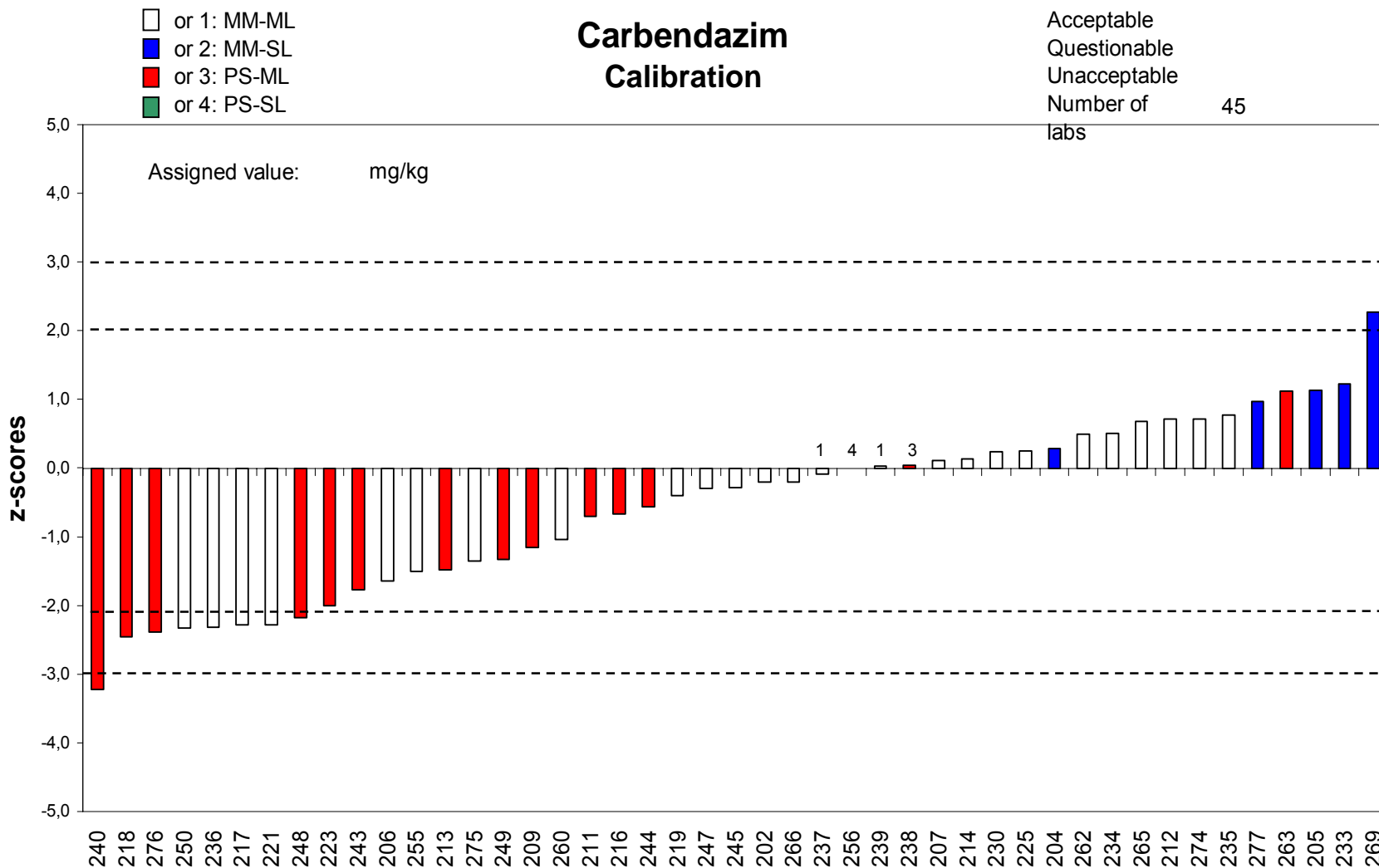
Pesticide	MM-ML	MM-SL	PS-ML	PS-SL	Standard addition
Azoxystrobin	36	13	12	1	2
Bifenthrin	39	12	12	1	
Alpha-cypermethrin	29	9	4	1	
Cypermethrin	17	5	7	1	
Carbendazim	25	5	14	1	2
Chlormequat	10	1	12		3
Chlorpyrifos-methyl	38	13	15	1	2
Difenconazole	28	11	8		1
Epoxiconazole	27	10	7		1
Iprodione	33	11	11	1	1
Malathion	32	10	12	1	1
Pirimicarb	27	11	8		1
Prochloraz	32	11	9	1	2
Spiroxamin	31	9	10		1
Trifloxystrobin	35	12	11	1	2

# Bifenthrin Calibration

- or 1: MM-ML
- or 2: MM-SL
- or 3: PS-ML
- or 4: PS-SL

Acceptable	92%
Questionable	8%
Unacceptable	2%
Number of labs	64

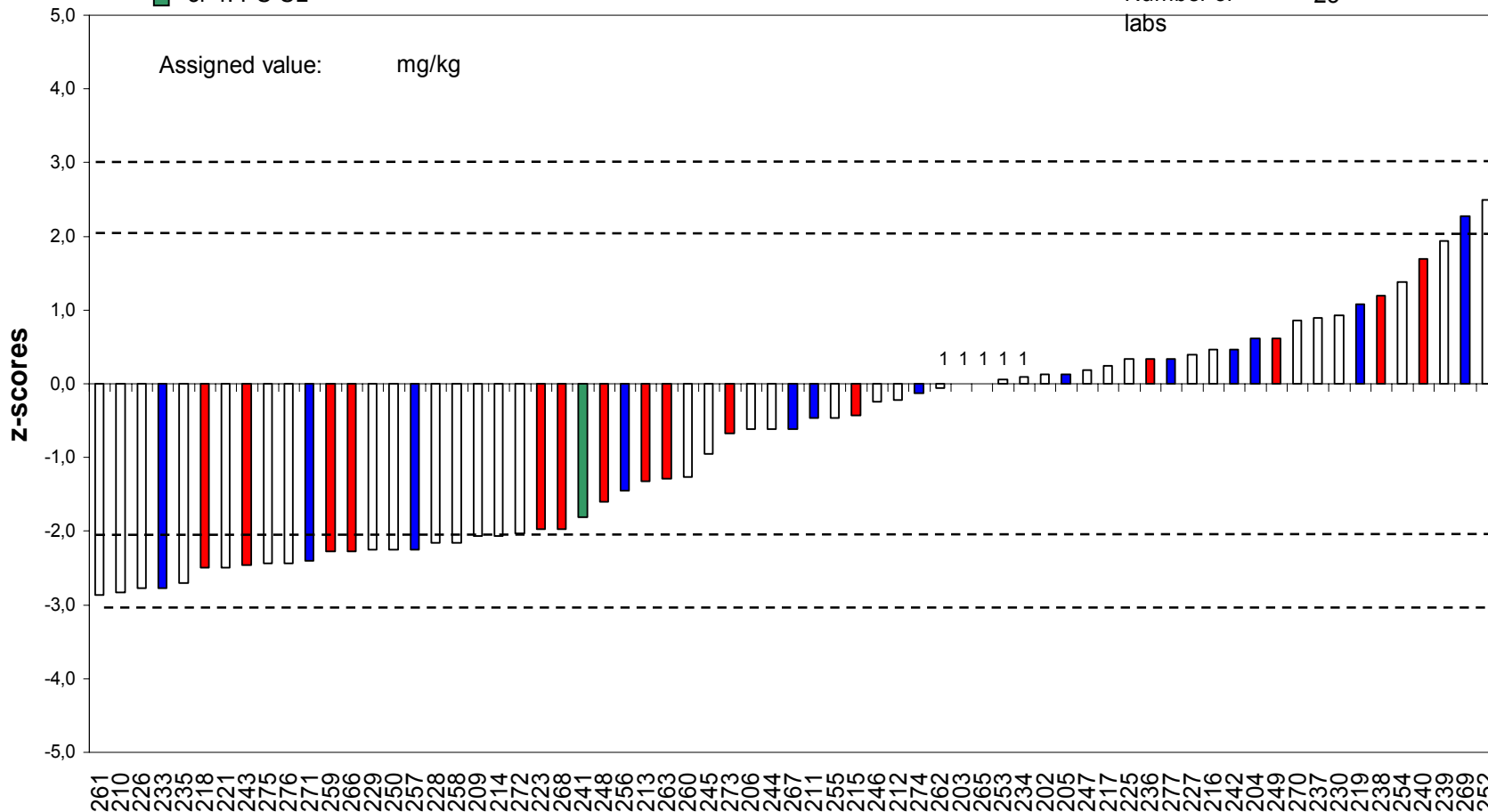




# Chlorpyrifos-methyl Calibration

- or 1: MM-ML
- or 2: MM-SL
- or 3: PS-ML
- or 4: PS-SL

Acceptable 1%  
 Questionable 0,130  
 Unacceptable  
 Number of 23  
 labs



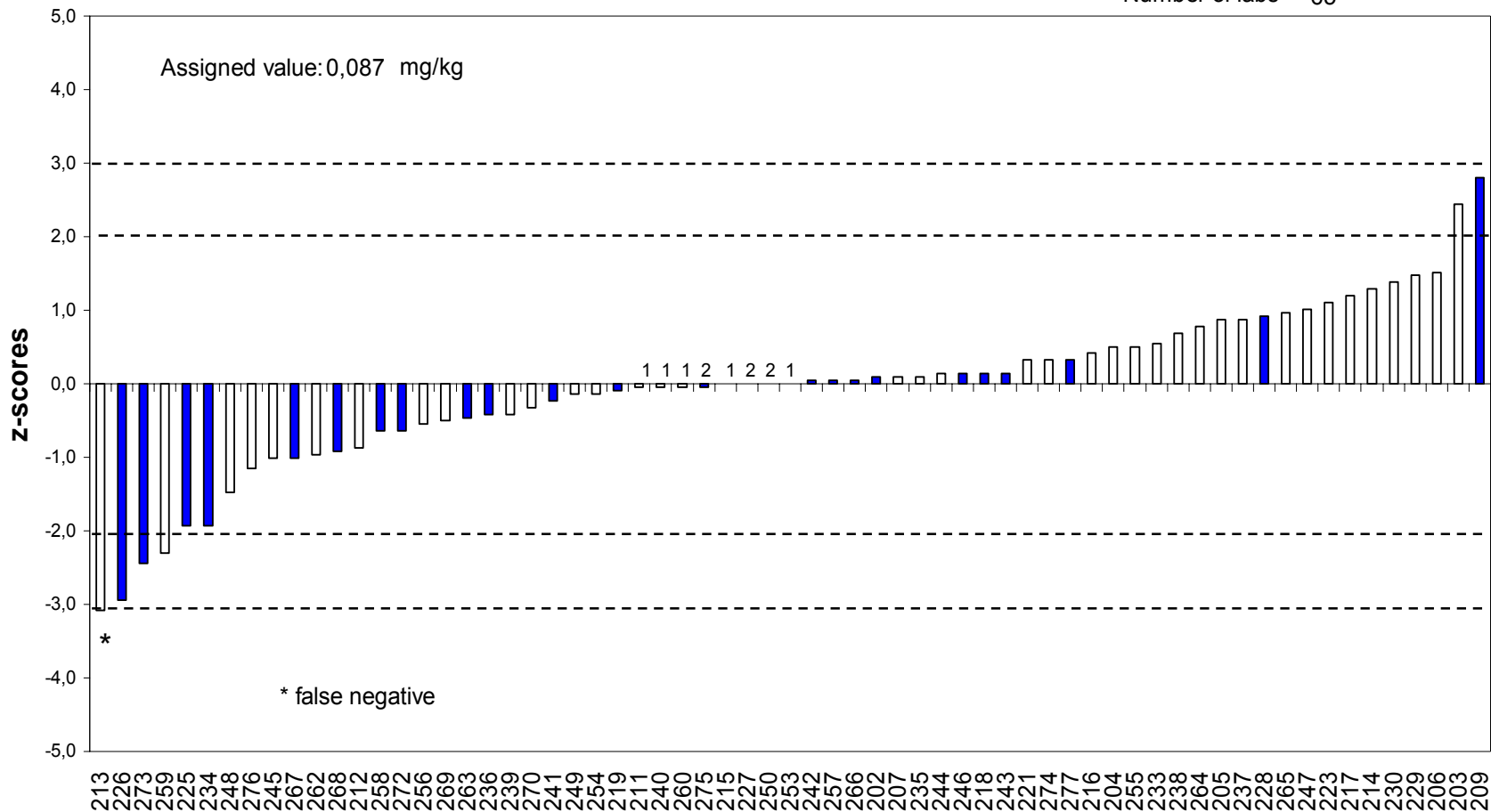
# Accreditation status

Pesticide	ACCREDITED	NOT ACCREDITED	% OF LABS ACCREDITED
Azoxystrobin	39	25	61
Bifenthrin	40	25	62
Alpha-cypermethrin	32	19	63
Cypermethrin	38	34	53
Carbendazim	33	16	67
Chloromequat	20	6	77
Chlorpyrifos-methyl	47	23	67
Difenconazole	28	21	57
Epoxiconazole	25	23	52
Iprodione	39	20	66
Malathion	39	22	64
Pirimicarb	42	23	65
Prochloraz	32	25	56
Spiroxamin	32	21	60
Trifloxystrobin	34	27	56

- or 1: Accredited
- or 2: Not accredited
- or 3: Not stated

## Bifenthrin Accreditation status

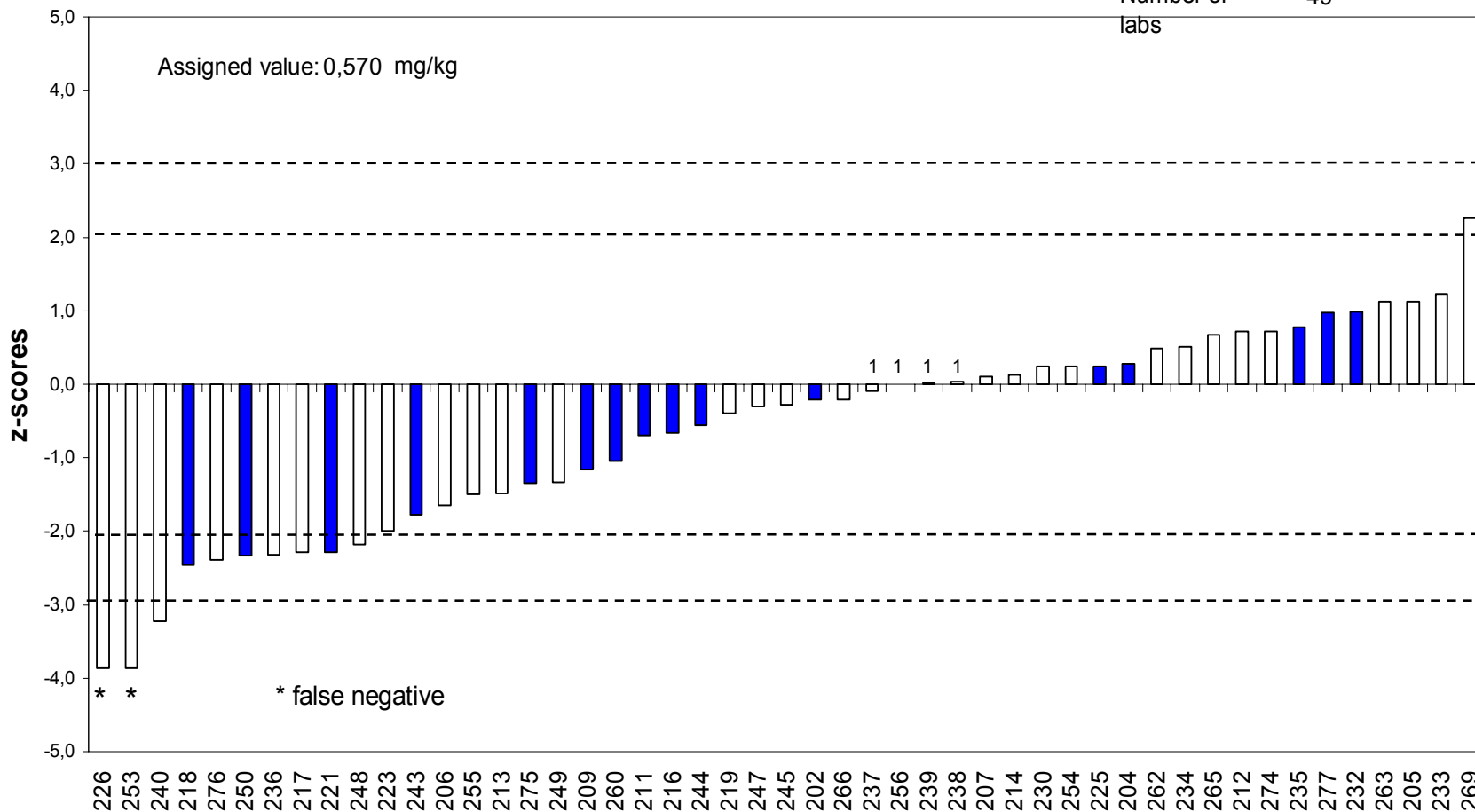
Acceptable	91%
Questionable	8%
Unacceptable	2%
Number of labs	65



- or 1: Accredited
- or 2: Not accredited
- or 3: not stated

## Carbendazim Accreditation status

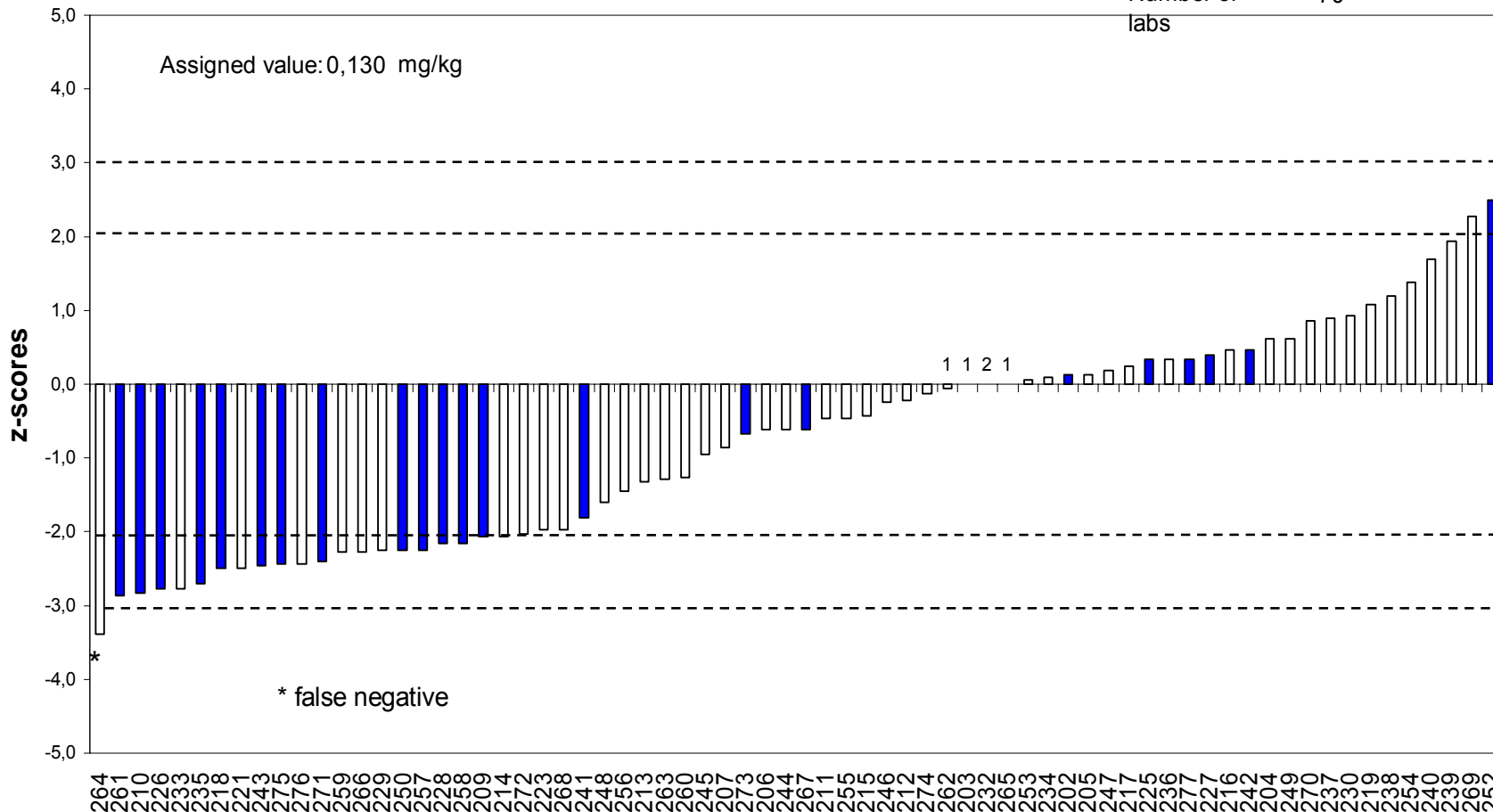
Acceptable 78%  
Questionable 16%  
Unacceptable 6%  
Number of 49  
labs



- or 1: Accredited
- or 2: Not accredited
- or 3: not stated

## Chlorpyrifos-methyl Accreditation status

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





# Summary

## Water addition

- The majority of the laboratories add water to the dry samples
- The results of the CF-PTC2 clearly shows how important it is to add water cereal samples before the extraction.
- This is true regardless of the extraction procedure (perhaps except for ASE).

## Clean up methods (summary cont.)

- GPC, DSPE and no clean up are the most frequently used methods
- Results obtained by these types of cleanup seems to be evenly distributed
- No clean up: Perhaps a slight indication of high recoveries for some compounds (bifenthrin)
- The addition of water overrules the effect of cleanup

## Calibration (summary cont.)

- No clear indication of connection between z-scores and the choice of calibration.
  - For some compounds calibration by MM-ML might result in high recoveries (bifenthrin)
  - Whereas for other compounds calibration by MM-SL might result in high recoveries (carbendazim)

## Accreditation status (summary cont.)

- In some cases the laboratories which were not accredited were slightly over represented among the laboratories with low Z-scores or low recoveries (bifenthrin, chlorpyrifos-methyl)
- For other compounds there were no differences in the results obtained whether the laboratories were accredited or not (carbendazim)

## Extraction method

- The most widely used extraction methods are:
  - QuEChERS
  - German
  - EN 12393
  - Luke
- It seems that QuEChERS and German method perform well for a wide range of compounds
- EN 12393 and Luke seems in general to result in Z-scores below zero

Thank you very much for your attention