EUPT-SRM13 Pesticide Residues in Soy Bean

M. Anastassiades
P. Schreiter / C. Wauschkuhn
A. Barth / G. Cerchia / D. Mack / S. Söhnholz

SELECTION OF COMMODITY & PESTICIDES TO BE SPIKED

I) COMMODITY Selection : Decision by EUPT-Sci. Committee meeting

II) PESTICIDE Selection; *Considering the following aspects …*

a) Pesticides included in **MACP or Working Document**:
   - ⇨ MACP: 2,4-D, Bromide, Chlormequat, Cyromazine, Ethephon, Glyphosate…
   - ⇨ WD: 2,4-DB, Chlorate, Glufosinate, Diquat …

b) Pesticides **applied in cultivation** of soy (and oily seeds in general)

c) Pesticides **found as residues** in soy (and oily seeds in general)

d) Overall **capabilities and interest of NRLs + OfLs**
   (feedback and communication with NRLs and OfLs, Cat A/B balance)

e) Analytical Matching of Pesticides (avoid too many methods)

EUPT-Scientific Committee

⇨ **Selection of Pesticides in Target Pesticide List (Survey via Excel sheet)**

EUPT-QC-Group

⇨ **Selection of pesticides to be spiked/approx. spiking levels**

⇨ **Division of pesticides into mandatory/optional**

EURL-SRM

EUPT-SC VOTING FOR PESTICIDE TARGET LIST

Compound	Analytical group	Analytical group	RD	MRM/SRM Full RD	Times in prev. EUPT-SRMs (#)	Details on presence in previous EUPT-SRMs	RELEVANCE Findings SOIA / NUTS etc.	RELEVANCE USAGE SOIA	RELEVANCE USAGE OILSEEDS, NUTS	
2,4-D	Acid	MRM/SRM	2,4-D (sum of 2,4-D, its salts, its esters and its conjugates, expressed as 2,4-D)	Full RD	7	SRM04 (mandatory; Qn: 27.5) | SRM04 (optional; Qn: 22.6) | SRM06 (mandatory; Qn: 22.1) | SRM07 (mandatory; Qn: 27.9) | SRM09 (mandatory; Qn: 18.7) | SRM10 (mandatory; Qn: 18.2) SRM12 (mandatory; Qn: 13.3)	high (but typically at low levels)	YES	YES	high
2,4-DB	Acid	MRM/SRM	2,4-DB (sum of 2,4-DB, its salts, its esters and its conjugates, expressed as 2,4-DB) (#)	SRM			no	YES	YES	Low
Bentazone	Acid	SRM	Bentazone (Sum of bentazone, its salts and 6-hydroxy (free and conjugated) and 8-hydroxy bentazone (free and conjugated), expressed as bentazone) #	SRM	1	SRM10 (optional; Qn: 18.5)	no	YES	YES	medium
Bromide (in-org.)	Individual	SRM	Bromide ion	SRM	3	SRM06 (mandatory; Qn: 6.6) | SRM07 (mandatory; Qn: 10.0) SRM12 (optional; Qn: 18.0)	(natural)	(natural)	(natural)	high
Carbofuran (sum, except 3-OH-CF)	QuEChERS with attn.	MRM	Carbofuran (sum of carbofuran (including any carbofuran generated from carbosulfan, benfuracarb or furathiocarb) and 3-OH carbofuran expressed as carbofuran) (#)	SRM	1	SRM12 (optional; Qn: 47.1; low level)	medium	no	YES	medium
Chlorate										
Chlormequ										
Cyromazine	PolarPos	SRM	Cyromazine	SRM	4	SRM07 (mandatory; Qn: 45.3) | SRM08 (mandatory; Qn: 27.2); SRM09 (optional; Qn: 28.8) | SRM11 (mandatory; Qn: 31.8)	no	no	no	medium
Diquat	PolarPos with attn.	SRM	Diquat	SRM	1	SRM08 optional, Qn: 28.6; only 10 numerical results, 4 FN |	low (but not analyzed much)	Yes (as dessicant)	YES	medium
Ethephon	Polarneg	SRM	Ethephon	SRM	4	SRM05 (mandatory; Qn: 25.0) | SRM06 (mandatory; Qn: 30.3) | SRM07 (mandatory; Qn: 27.7) | SRM10 (mandatory; Qn: 30.8)	medium	no	no	high
Fenoxaprop	acid	MRM/SRM	Fenoxaprop-P	MRM/SRM			no	YES	no	Low

Approved EU (general)	Monitoring (Regulation / Working Document)	Notes	Tendency on inclusion in Target Pest List (by EURL-SRM) Proposal by Organizers	POINTS COUNT Total Pts = YES-NO (click above to see notes)	NOTES by Advisory Group	FINAL SELECTION BASED ON VOTING AND MACP Status	
Approved	MACP - Plant (2017 ff)	high relevance	YES	10		Candidate	mandatory
Approved	WD - Interest for Cumulative Risk assessment	high relevance for matrix group	YES	8		Candidate	Optional
Approved	/	high relevance for the entire group (not soy)	YES	8	PP: the compound is not relevant for soya bean and is not in the MACP/WD	Candidate	Optional
Matr not Appr. but natural Levels	MACP - Plant (2017 ff)	fumigation and natural	YES	9		Candidate	mandatory
Not Approved	MACP - Plant (2017 ff)	relevant, important compound due to toxicity need to test analysis of new RD;	YES	6		Candidate	Optional
							Optional
							mandatory
Approved	MACP - Plant (2017 ff)	little relevance for matrix group	No	4		borderline	mandatory
Approved	WD - Plant	High relevance but analytically challenging	?	4	DM: optional; important to encourage labs (not too many labs in routine) only one PT so far; not too many PT providers	borderline	Optional
Approved	MACP - Plant (2017 ff)	little relevance for this matrix group	No	5		Candidate	mandatory
Approved	/	some relevance	?	6		Candidate	Optional

Considering different aspects on:
use, residue findings, MACP inclusion, lab capabilities, method fits
…

EUPT-SRM13 ORGANISATION

Registration for EUPT-SRM13:

26 Feb. – 16 March 2018

Sample Shipment:

23 April, 2018

Results Submission:

24 May→29 May, 2018
(subpage 3 till 08.June, 2018)

Preliminary Report:

19 June, 2018

EURL-SRM
EU Reference Laboratories for Residues of Pesticides
Single Residue Methods

CALENDAR for the EUPT – SRM13

Soybeans

(released on 23 January, 2018)

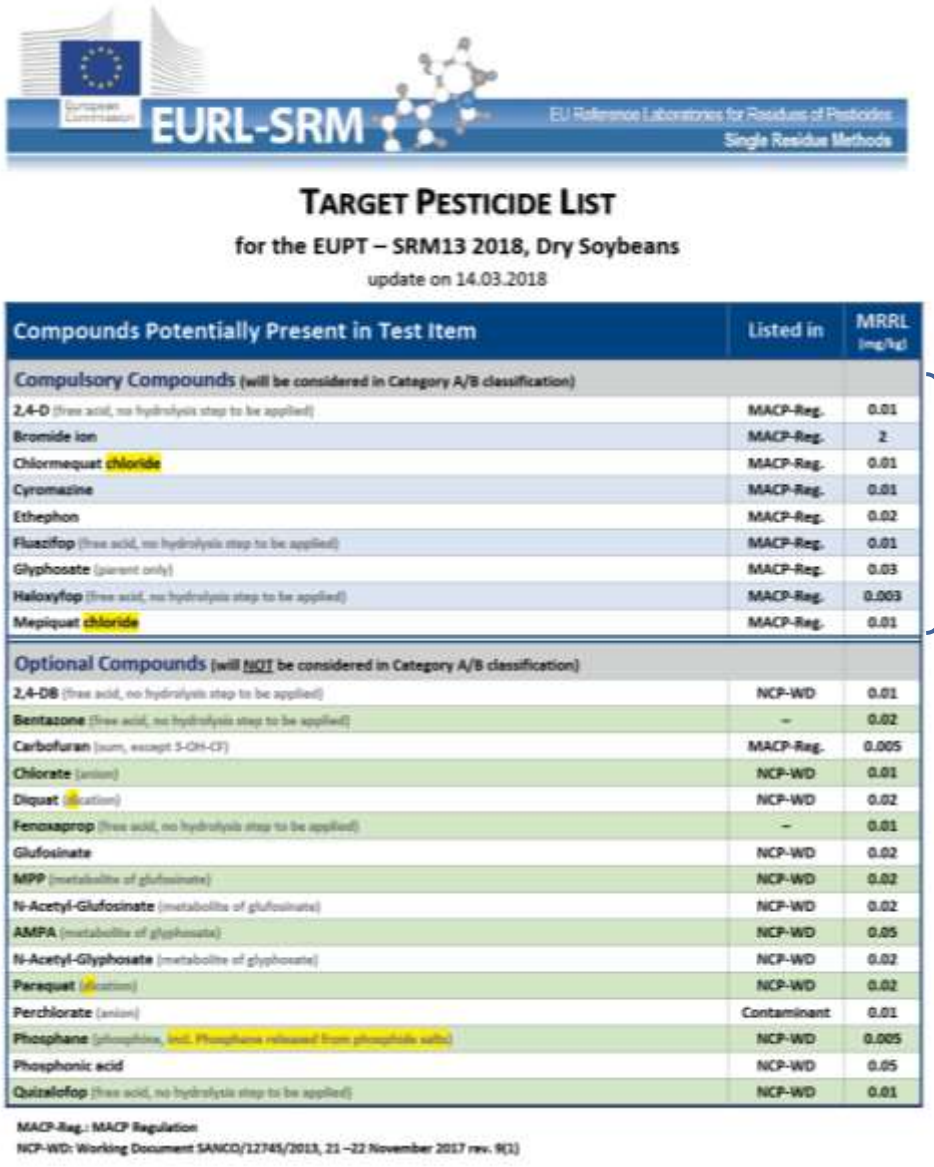
Activity	Who?	Dates
Opening of the EUPT-SRM13 Website with links to all relevant documents (Calendar, Target Pesticides List, General Protocol)	EURL-SRM	23 Jan., 2018
Registration via "EUPT-Registration Website" (Note: Obliged Laboratories MUST enter this Website and either register or give **explanations for non-participation**)	**All Laboratories interested in participation and all obliged labs even if not interested**	**26 Feb. – 16 March 2018**
Dispatch of EUPT-SRM13-Specific Protocol	EURL-SRM	April 2018
Preparation of EUPT-SRM13-Test Item (preliminary tests Spiking / Homogenization)	EURL-SRM	March 2018 – April 2018
Homogeneity Tests	EURL-SRM	March 2018 – April 2018
Stability Tests	EURL-SRM	April – June 2018
Shipment of EUPT-SRM13 Test Item (+reminder of upcoming parcel arrival)	EURL-SRM	**23 April, 2018**
Confirmation of sample Receipt and acceptance via "EUPT-SRM13 Result Submission Website", (Sub-Page II)	**Participating Labs**	**within 48 h of receipt**
Result Submission (Pesticide scope, Results, Method Info) in "EUPT-SRM13 Result Submission Website", (Sub-Pages 1 – 3)	**Participating Labs**	**30 April – 29 May 2018**
Preliminary Report (only compilation of results and preliminary assigned values)	EURL-SRM	June 2018
EUPT Evaluation Meeting	EUPT-SC, DG-SANTE	–
Survey to collect reasons for underperformance and missing information on methods	EURL-SRM / **Participating Labs**	June / July 2018
Final Report	EURL-SRM	Dec. 2018

REMARK: Please note that the dates mentioned above may be subject to minor **changes**. In the case of changes the participants will be informed via e-mail. **But please, still check periodically our website for possible updates** in case the email does not get through to you.
Contact: eurl-srm@cvuas.bwl.de

EURL-SRM TARGET PESTICIDES LIST

	In Target List
Compulsory	9
Optional*	16

* Optional = not considered in A/B lab-categorization by scope



EURL-SRM — EU Reference Laboratories for Residues of Pesticides — Single Residue Methods

TARGET PESTICIDE LIST

for the EUPT – SRM13 2018, Dry Soybeans

update on 14.03.2018

Compounds Potentially Present in Test Item	Listed in	MRRL (mg/kg)
Compulsory Compounds (will be considered in Category A/B classification)		
2,4-D (free acid, no hydrolysis step to be applied)	MACP-Reg.	0.01
Bromide ion	MACP-Reg.	2
Chlormequat chloride	MACP-Reg.	0.01
Cyromazine	MACP-Reg.	0.01
Ethephon	MACP-Reg.	0.02
Fluazifop (free acid, no hydrolysis step to be applied)	MACP-Reg.	0.01
Glyphosate (parent only)	MACP-Reg.	0.03
Haloxyfop (free acid, no hydrolysis step to be applied)	MACP-Reg.	0.003
Mepiquat chloride	MACP-Reg.	0.01
Optional Compounds (will NOT be considered in Category A/B classification)		
2,4-DB (free acid, no hydrolysis step to be applied)	NCP-WD	0.01
Bentazone (free acid, no hydrolysis step to be applied)	–	0.02
Carbofuran (sum, except 3-OH-CF)	MACP-Reg.	0.005
Chlorate (anion)	NCP-WD	0.01
Diquat (dication)	NCP-WD	0.02
Fenoxaprop (free acid, no hydrolysis step to be applied)	–	0.01
Glufosinate	NCP-WD	0.02
MPP (metabolite of glufosinate)	NCP-WD	0.02
N-Acetyl-Glufosinate (metabolite of glufosinate)	NCP-WD	0.02
AMPA (metabolite of glyphosate)	NCP-WD	0.05
N-Acetyl-Glyphosate (metabolite of glyphosate)	NCP-WD	0.02
Paraquat (dication)	NCP-WD	0.02
Perchlorate (anion)	Contaminant	0.01
Phosphane (phosphine, incl. Phosphane released from phosphide salts)	NCP-WD	0.005
Phosphonic acid	NCP-WD	0.05
Quizalofop (free acid, no hydrolysis step to be applied)	NCP-WD	0.01

Compulsory

Optional

MACP-Reg.: MACP Regulation

NCP-WD: Working Document SANCO/12745/2013, 21 –22 November 2017 rev. 9(1)

EURL-SRM

TARGET PESTICIDES LIST

	On Target List	Spiked*	Spiking details	Sum
Compulsory	**9**	1. Bromide ion 2. Cyromazine 3. Fluazifop 4. Glyphosate 5. Mepiquat 6. Fluazifop 7. Haloxyfop	**Portion of intact soy beans spiked in LAB with compounds in solution milled and mixed with other material**	**7**
Optional	**16**	1. Diquat 2. Glufosinate 3. MPP 4. N-Acetyl-Glyphosate 5. Perchlorate 6. Phosphonic acid 7. Quizalofop 8. 2,4-DB 9. Quizalofop		**10 (+1)**
		10. Phsophine I 10a. Phosphine II	**Portion of intact material treated with PH_3 in professional FUMIGATION PLANT milled and mixed with other material**	
TOTAL	**25**			**17 (+1)**

EURL-SRM

PREPARATION OF TEST ITEM

EURL-SRM

HOMOGENEITY TEST

COMPULSORY Compounds

	Bromide ion	Cyromazine	Fluazifop free acid	Glyphosate	Haloxyfop free acid	Mepiquat chloride
sample	Concentration [mg/kg]					
24	14.2 / 15.3	0.098 / 0.116	0.053 / 0.050	0.840 / 0.938	0.017 / 0.017	0.121 / 0.136
36	14.3 / 16.5	0.112 / 0.121	0.050 / 0.051	0.923 / 0.973	0.016 / 0.018	0.130 / 0.135
47	14.8 / 14.0	0.113 / 0.106	0.045 / 0.048	1.017 / 0.973	0.016 / 0.015	0.131 / 0.124
66	15.9 / 14.6	0.099 / 0.109	0.054 / 0.049	0.885 / 0.891	0.017 / 0.016	0.115 / 0.128
77	14.4 / 14.9	0.108 / 0.108	0.052 / 0.053	0.914 / 0.999	0.017 / 0.017	0.128 / 0.134
90	15.1 / 15.7	0.105 / 0.108	0.050 / 0.047	0.866 / 0.936	0.016 / 0.016	0.125 / 0.132
110	12.2 / 13.0	0.101 / 0.094	0.048 / 0.048	0.842 / 0.814	0.017 / 0.016	0.105 / 0.113
122	13.7 / 15.3	0.100 / 0.104	0.049 / 0.051	0.825 / 1.029	0.016 / 0.017	0.121 / 0.125
142	14.2 / 13.6	0.113 / 0.106	0.049 / 0.047	0.969 / 0.938	0.016 / 0.015	0.132 / 0.128
167	13.9 / 16.8	0.105 / 0.116	0.049 / 0.048	0.922 / 0.976	0.016 / 0.016	0.125 / 0.141
mean	**14.6**	**0.107**	**0.049**	**0.924**	**0.016**	**0.126**
s_{sam}^2	2.34×10^{-1}	6.76×10^{-6}	2.73×10^{-6}	4.58×10^{-4}	4.34×10^{-8}	2.82×10^{-5}
c	3.30×10^{0}	1.62×10^{-4}	2.89×10^{-5}	1.27×10^{-2}	3.27×10^{-6}	2.15×10^{-4}
$s_{sam}^2 < c$	passed	passed	passed	passed	passed	passed

EURL-SRM

HOMOGENEITY TEST

OPTIONAL Compounds-1

	2.4-DB free acid	Diquat dication	Glufosi-nate	MPP	N-Acetyl-Glyphosate	Perchlorate	Phosphonic acid	Quizalofop free acid
sample	Concentration [mg/kg]							
11	0.187 / 0.192	1.60 / 1.20	0.195 / 0.211	0.164 / 0.189	0.696 / 0.769	0.099 / 0.109	1.87 / 2.08	0.062 / 0.061
25	0.181 / 0.187	1.50 / 1.60	0.211 / 0.255	0.187 / 0.197	0.832 / 0.880	0.104 / 0.117	2.16 / 2.20	0.056 / 0.062
38	0.163 / 0.167	1.30 / 1.30	0.181 / 0.192	0.179 / 0.178	0.772 / 0.817	0.108 / 0.100	2.08 / 2.03	0.057 / 0.056
43	0.194 / 0.164	1.50 / 1.50	0.212 / 0.202	0.171 / 0.177	0.725 / 0.792	0.103 / 0.106	1.93 / 2.01	0.063 / 0.060
80	0.183 / 0.185	1.40 / 1.60	0.216 / 0.174	0.172 / 0.188	0.739 / 0.821	0.096 / 0.111	1.90 / 2.09	0.063 / 0.061
90	0.179 / 0.169	1.40 / 1.40	0.213 / 0.207	0.174 / 0.179	0.739 / 0.750	0.104 / 0.106	1.95 / 2.06	0.060 / 0.054
96	0.172 / 0.179	1.30 / 1.40	0.160 / 0.167	0.155 / 0.151	0.654 / 0.633	0.095 / 0.092	1.77 / 1.67	0.056 / 0.057
157	0.173 / 0.184	1.70 / 1.60	0.149 / 0.180	0.157 / 0.175	0.666 / 0.779	0.100 / 0.100	1.87 / 2.01	0.056 / 0.059
187	0.166 / 0.180	1.50 / 1.30	0.213 / 0.184	0.179 / 0.173	0.794 / 0.762	0.110 / 0.104	2.09 / 2.01	0.059 / 0.055
195	0.165 / 0.176	1.50 / 1.50	0.182 / 0.237	0.171 / 0.192	0.716 / 0.835	0.095 / 0.106	1.88 / 2.21	0.057 / 0.055
mean	0.177	1.46	0.197	0.175	0.759	0.103	1.99	0.058
s_{sam}^2	1.44×10^{-5}	3.41×10^{-3}	2.25×10^{-4}	5.90×10^{-5}	1.79×10^{-3}	3.91×10^{-6}	7.33×10^{-3}	2.06×10^{-6}
c	4.11×10^{-4}	3.44×10^{-2}	8.71×10^{-4}	4.19×10^{-4}	8.58×10^{-3}	1.48×10^{-4}	5.46×10^{-2}	4.24×10^{-5}
$s_{sam}^2 < c$	passed	passed	passed	passed	passed	passed	passed	passed

HOMOGENEITY TEST

OPTIONAL Compounds-2

	Phosphane (Test Item)		Phosphane(PH3-sample)
sample	Concentration [mg/kg]	sample	Concentration [mg/kg]
1	0.187 / 0.189	1	0.068 / 0.082
6	0.17 / 0.191	5	0.059 / 0.068
13	0.178 / 0.185	8	0.077 / 0.06
16	0.175 / 0.192	11	0.079 / 0.064
31	0.167 / 0.183	17	0.064 / 0.078
100	0.184 / 0.18	21	0.063 / 0.067
114	0.177 / 0.197	26	0.073 / 0.059
140	0.17 / 0.185	41	0.057 / 0.06
154	0.176 / 0.192	48	0.062 / 0.069
172	0.186 / 0.191	51	0.073 / 0.076
mean	0.183	mean	0.068
S_{sam}^2	0 × 10-0	S_{sam}^2	0×10^{-0}
c	4.51 × 10-4	c	1.14×10^{-4}
$S_{sam}^2 < C$	passed	$S_{sam}^2 < C$	passed

EURL-SRM STABILITY TEST

COMPULSORY Compounds

Sample	Bromide ion [mg/kg]			Cyromazine [mg/kg]			Fluazifop (free acid) [mg/kg]		
	03.05.2018	22.05.2018	18.06.2018	03.05.2018	22.05.2018	18.06.2018	25.04.2018	17.05.2018	07.06.2018
77	14.7	13.6	14.1	0.108	0.100	0.112	0.053	0.048	0.050
110	12.6	13.9	14.0	0.098	0.106	0.109	0.048	0.051	0.050
142	13.9	14.7	14.2	0.110	0.108	0.111	0.048	0.050	0.047
Mean	**13.7**	**14.1**	**14.1**	**0.105**	**0.105**	**0.111**	**0.050**	**0.050**	**0.049**
% Difference (vs. 1st Analysis)	—	**2.37%**	**2.78%**	—	**-0.38%**	**5.29%**	—	**0.45%**	**-1.73%**
Diff (mean)		**0.3**	**0.4**		**0.000**	**0.006**		**0.000**	**0.001**
0,3* FFP-SD		**1**	**1**		**0.008**	**0.008**		**0.004**	**0.004**
Judgement		**passed**	**passed**		**passed**	**passed**		**passed**	**passed**

Sample	Glyphosate [mg/kg]			Haloxyfop (free acid) [mg/kg]			Mepiquat chloride [mg/kg]		
	03.05.2018	22.05.2018	18.06.2018	25.04.2018	17.05.2018	07.06.2018	03.05.2018	22.05.2018	18.06.2018
77	0.957	0.940	0.954	0.017	0.017	0.017	0.131	0.122	0.133
110	0.828	0.961	0.869	0.016	0.016	0.018	0.109	0.134	0.129
142	0.954	0.991	0.977	0.016	0.015	0.018	0.130	0.128	0.131
Mean	**0.913**	**0.964**	**0.933**	**0.016**	**0.016**	**0.017**	**0.123**	**0.128**	**0.131**
% Difference (vs. 1st Analysis)	—	**5.60%**	**2.22%**	—	**0.12%**	**7.12%**	—	**3.76%**	**6.19%**
Diff (mean)		**0.051**	**0.020**		**0.000**	**0.001**		**0.005**	**0.008**
0,3* FFP-SD		**0.068**	**0.068**		**0.001**	**0.001**		**0.009**	**0.009**
Judgement		**passed**	**passed**		**passed**	**passed**		**passed**	**passed**

EURL-SRM STABILITY TEST

OPTIONAL Compounds

Sample	2.4-DB (free acid) [mg/kg]			Diquat dication [mg/kg]			Glufosinate [mg/kg]			MPP [mg/kg]			N-Acetyl-Glyphosate [mg/kg]		
	25.04.2018	17.05.2018	07.06.2018	03.05.2018	22.05.2018	18.06.2018	03.05.2018	22.05.2018	18.06.2018	03.05.2018	22.05.2018	18.06.2018	03.05.2018	22.05.2018	18.06.2018
77	0.184	0.179	0.164	1.52	1.34	1.43	0.195	0.197	0.210	0.180	0.172	0.173	0.780	0.752	0.812
110	0.176	0.187	0.168	1.37	1.35	1.47	0.164	0.170	0.167	0.153	0.172	0.159	0.644	0.772	0.697
142	0.173	0.183	0.164	1.38	1.38	1.37	0.199	0.184	0.180	0.176	0.179	0.164	0.778	0.797	0.717
Mean	**0.177**	**0.183**	**0.165**	**1.42**	**1.36**	**1.42**	**0.186**	**0.183**	**0.186**	**0.170**	**0.174**	**0.165**	**0.734**	**0.773**	**0.742**
% Difference (vs. 1st Analysis)	—	**3.12%**	**-7.01%**	—	**-4.49%**	**-0.05%**	—	**-1.26%**	**0.00%**	—	**2.66%**	**-2.64%**	—	**5.37%**	**1.06%**
Diff (mean)		**0.006**	**0.012**		**0.06**	**0.00**		**0.002**	**0.000**		**0.005**	**0.004**		**0.039**	**0.008**
0,3* FFP-SD		**0,013**	**0,013**		**0,11**	**0,11**		**0,014**	**0,014**		**0,013**	**0,013**		**0,055**	**0,055**
Judgement		**passed**	**passed**		**passed**	**passed**		**passed**	**passed**		**passed**	**passed**		**passed**	**passed**

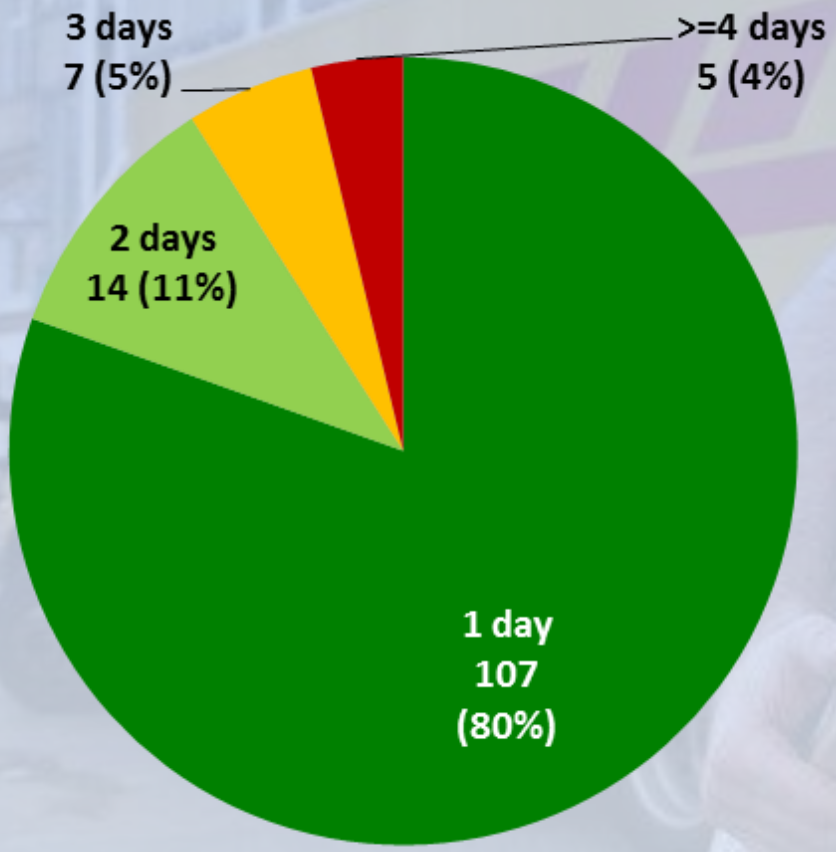
Sample	Perchlorate [mg/kg]			Phosphonic acid [mg/kg]			Quizalofop (free acid) [mg/kg]			Phosphane [mg/kg]			Phosphane PH3 [mg/kg]		
	03.05.2018	22.05.2018	18.06.2018	03.05.2018	22.05.2018	18.06.2018	25.04.2018	17.05.2018	07.06.2018	20.06.2018	19.07.2018	24.09.2018	28.05.2018	19.06.2018	18.07.2018
77 (6#/5*)	0.103	0.095	0.107	2.00	1.89	2.01	0.062	0.062	0.055	0.180	0.151	0.188	0.063	0.069	0.076
110 (16#/17*)	0.093	0.103	0.107	1.72	1.99	1.88	0.056	0.057	0.060	0.183	0.149	0.187	0.071	0.065	0.086
142 (31#/26*)	0.107	0.104	0.110	2.05	2.00	1.93	0.057	0.056	0.059	0.177	0.147	0.190	0.066	0.074	0.078
Mean	**0.101**	**0.101**	**0.108**	**1.92**	**1.96**	**1.94**	**0.058**	**0.059**	**0.058**	**0.180**	**0.149**	**0.188**	**0.067**	**0.069**	**0.080**
% Difference (vs. 1st Analysis)	—	**-0.38%**	**6.49%**	—	**1.90%**	**0.85%**	—	**0.26%**	**-1.21%**	—	**-17%**	**4.3%**	—	**3.83%**	**20.0%**
Diff (mean)		**0.000**	**0.007**		**0.04**	**0.02**		**0.000**	**0.001**		**0.031**	**0.008**		**0.003**	**0.003**
0,3* FFP-SD		**0.008**	**0.008**		**0.14**	**0.14**		**0.004**	**0.004**		**0.014**	**0.014**		**0.005**	**0.005**
Judgement		**passed**	**passed**		**passed**	**passed**		**passed**	**passed**		failed	**passed**		**passed**	failed

All stability test samples were extracted at the indicated day and measured alltogether at the end.

EURL-SRM

STABILITY DURING SHIPPING

Shipment Duration



- 91 % within 2 days
- 3 days: holiday / remote (incl. 3rd countries)
- 4 days: delays in customs clearance (one 3rd lab > 1 month due to strike!)
- No noticable negative influence on the results from laboratories having received the sample after > 4 days

PARTICIPATING LABS / COUNTRIES

EU countries on behalf of	Registered for EUPT-SRM13	
	Total	NRL-SRM
AT	1	1
BE; NL	1	
BE	6	1
BE; BG; FR; LU	1	
BG	1	1
CY	1	1
CZ	3	1
DE	20	1
DE; MT	1	
DK	1	1
EE	2	1
ES	13	2
ES; MT	1	
FI	2	2
FR	8	1
GR	3	2
HR	3	
HU	5	1
IE	1	1
IT	9	0
IT; MT	1	
LT	2	1
LU	1	1
LV	1	1
NL	2	1
PL	3	1
PO	2	
PT	1	1
RO	1	
SE	2	1
SI	2	1
SK	1	1
UK; MT	1	1
UK	2	
EU Total	**105**	**27**

EFTA-Countries	Registered for EUPT-SRM13
CH	**3**
NO	**1**
EFTA-Total	**4**

EU Candidate & 3rd countries	Registered for EUPT-SRM13
BR	1
BY	1
PE	1
RS	2
SG	1
TH	1
CR	1
EU Candidate & 3rd Total	**7**

MT
subcontracts FERA (UK) as Proxy-NRL
+ Eurofins (DE) + IZSLER (IT) + LAGV (ES) for routine controls

Eurofins Lab Zeeuws-Vlaanderen (NL): Subcontracted by BE, NL

Primoris (BE):Subcontracted by BE, BG, FR, LU

Countries with no NRL-SRMs participating:
HR: *"NRL-SRM not yet appointed"*
IT: *Instruments out of order*

EURL-SRM

PARTICIPATING LABS / COUNTRIES

		Labs submitting results	Registered WITHOUT submitting results
EU		105	5*
EFTA		4	-
3rd Countries + EU Candidates		7	1+
	SUM	116	6

* Technical problems; +: Sample arrived after submission deadline

EURL-SRM

FREQUENCY OF ANALYSIS

Compulsory compounds

Present in Test Item

Compound	No. of Labs targeting (% out of 109* labs)
Fluazifop	86 (79 %)
Mepiquat	86 (79 %)
Glyphosate	83 (76 %)
Haloxyfop	81 (74 %)
Cyromazine	79 (72 %)
Bromide ion	62 (57 %)

NOT present in Test Item

Compound	No. of Labs targeting (% out of 109* labs)
2,4-D	88 (81 %)
Chlormequat	88 (81 %)
Ethephon	75 (69 %)

≥ 75 %
≥ 50-74 %
25-49 %
<25 %

*: 105 EU + 4 EFTA labs submitting results

Optional Compounds

Present in Test Item

Compound	No. of Labs targeting (% out of 109* labs)
Quizalofop	62 (57 %)
Perchlorate	55 (50 %)
2,4-DB	52 (48 %)
Phosphonic acid	45 (41 %)
Glufosinate	44 (40 %)
Diquat	30 (28 %)
MPP	25 (23 %)
N-Acetyl-Glyphosate	23 (21 %)
Phsophine	11 (10 %)
Phosphine (PH3)	11 (10 %)

NOT present in Test Item

Compound	No. of Labs targeting (% out of 109* labs)
Carbofuran	77 (71 %)
Bentazone	73 (67 %)
AMPA	56 (51 %)
Chlorate	56 (51 %)
Fenoxaprop	41 (38 %)
Paraquat	29 (27 %)
N-Acetyl-Glufosinate	23 (21 %)

Coverage

≥ 75 %
≥ 50-74 %
25-49 %
<25 %

*: 105 EU + 4 EFTA labs submitting results

EURL-SRM

ANALYTES FOUND IN BLANK MATERIAL

EU+EFTA

No significant findings in Blank Material

Pesticide	MRRL	RL	Konz-Blank
Chlormequat	0.01	0.01	**<0.01**
		Not reported	**<RL**
Ethephon	0.02	0.01	**<RL**
		0.1	**<0.1**
2,4-DB	0.01	0.01	**<RL**
Chlorate	0.01	0.01	**<0.01**
		Not reported	**<RL**
Diquat	0.02	0.01	**<0.01**
		0.05	**< 0.05**
Glufosinate	0.02	0.01	**< 0.01**
		0.01	**<0.01**
		0.02	**<0.02**
		Not reported	**<RL**
MPP	0.02	0.01	**< 0.01**
		0.02	**<0.02**
		Not reported	**<RL**
N-Acetyl-Gluf.	0.02	0.02	**<0.02**
Paraquat	0.02	0.02	**<0.02**

Pesticide	MRRL	RL	Konz-Blank
Chlormequat	0.01	0.01	**<0.01**
		Not reported	**<RL**
Ethephon	0.02	0.01	**<RL**
		0.1	**<0.1**
2,4-DB	0.01	0.01	**<RL**
Chlorate	0.01	0.01	**<0.01**
		Not reported	**<RL**
Diquat	0.02	0.01	**<0.01**
		0.05	**< 0.05**
Glufosinate	0.02	0.01	**< 0.01**
		Not reported	**<0.01**
		0.02	**<0.02**
		Not reported	**<RL**
MPP	0.02	0.01	**< 0.01**
		0.02	**<0.02**
		Not reported	**<RL**

Bromide reported by 17 labs in blank - median value: 0.75 mg/kg

EURL-SRM

FALSE NEGATIVES

False Negatives (FN), COMPULSORY COMPOUNDS = 5

EU+EFTA

	Compound	MRRL [mg/kg]	Assigned Value [mg/kg]	No. FNs	Lab Code	RL [mg/kg]
COMPULSORY	**Bromide ion**	2	15.3	1	**65**	12.5
	Cyromazine	0.01	0.097	1	**2**	0.01
	Fluazifop	0.01	0.049	1	**90**	0.005
	Mepiquat	0.01	0.124	2	**2**	0.01
					66	0.01

EURL-SRM

FALSE NEGATIVES

False Negatives (FN), OPTIONAL COMPOUNDS = 19

EU+EFTA

	Compound	MRRL [mg/kg]	AV [mg/kg]	No. FNs	Lab Code	RL [mg/kg]
OPTIONAL	2,4-DB	0.01	0.183	2	55	0.01
					109	0.01
	Diquat	0.02	1.701	1	109	0.02
	Glufosinate	0.02	0.192	3	55	0.04
					89	0.02
					105	0.1
	MPP	0.02	0.188	1	109	0.02
	N-Acetyl-Glyphosate	0.02	0.835	5	45	0.02
					55	0.04
					76	—
					89	0.02
					109	0.02
	Perchlorate	0.01	0.100	2	2	0.01
					109	0.01
	Phosphonic acid	0.05	1.864	3	11	0.05
					85	0.1
					97	0.1
	Quizalofop	0.01	0.052	2	47	—
					66	0.01

EURL-SRM

FALSE POSITIVES

EU+EFTA

False Positives (FP) = 3

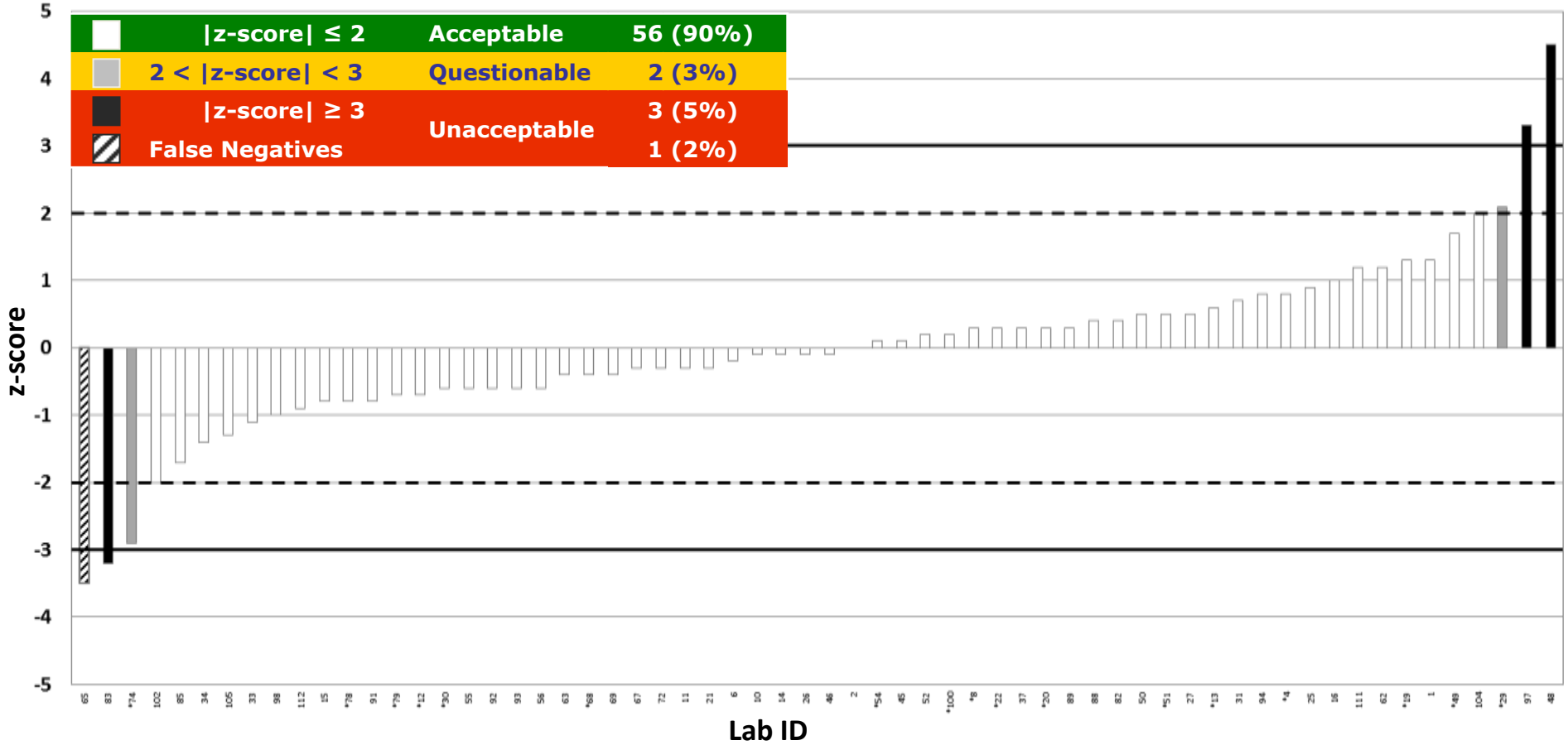
	Compound	Lab Code	MRRL [mg/kg]	RL [mg/kg]	Results [mg/kg]	Judgement
COMPULSORY	Ethephon	41	0.02	0.01	0.368	FP
OPTIONAL	Carbofuran	7	0.005	—	0.0028	not FP
	Chlorate	67	0.01	0.005	0.0043	not FP
	N-Acetyl-Glufosinate	45	0.02	0.02	1.26	FP
	AMPA	41	0.05	0.01	0.078	FP
		98	0.05	0.01	0.002	not FP

EURL-SRM

BROMIDE ION

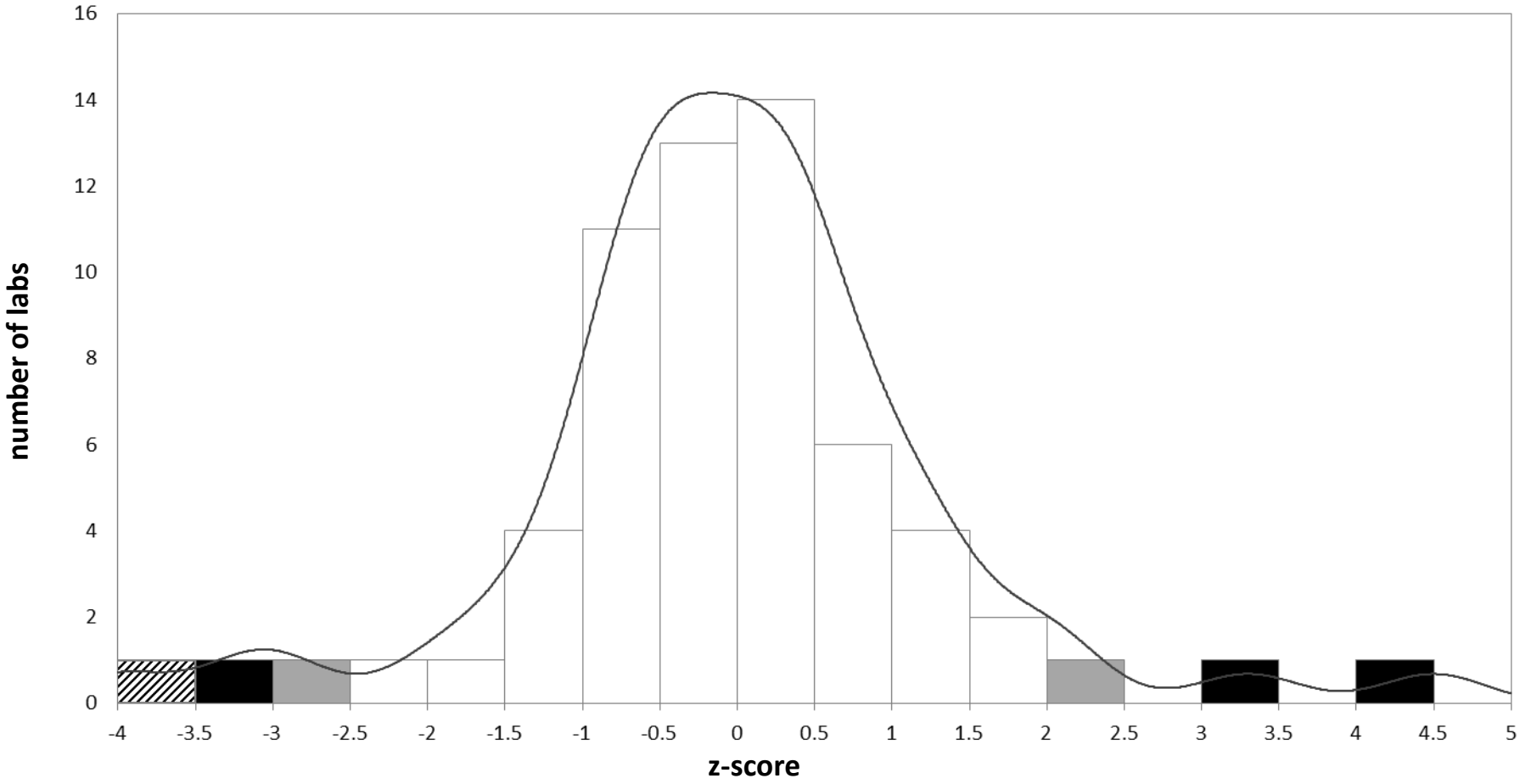
Bromide ion

Results	62
False Neg.	1
AV	15.4 [mg/kg]
CV*	24.0 %
MRRL	2 [mg/kg]



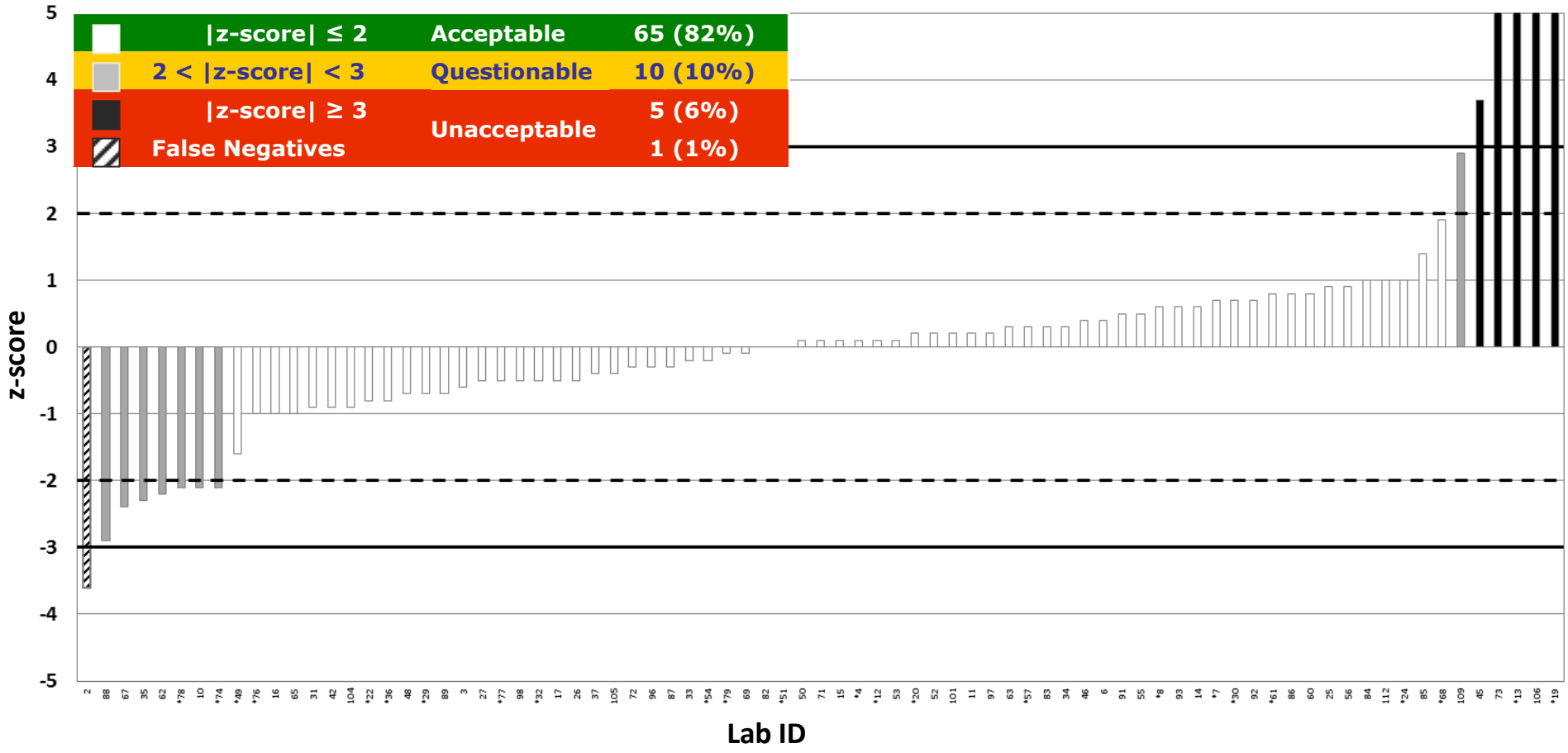
Bromide ion

Results	62
False Neg.	1
AV	15.4 [mg/kg]
CV*	24.0 %
MRRL	2 [mg/kg]



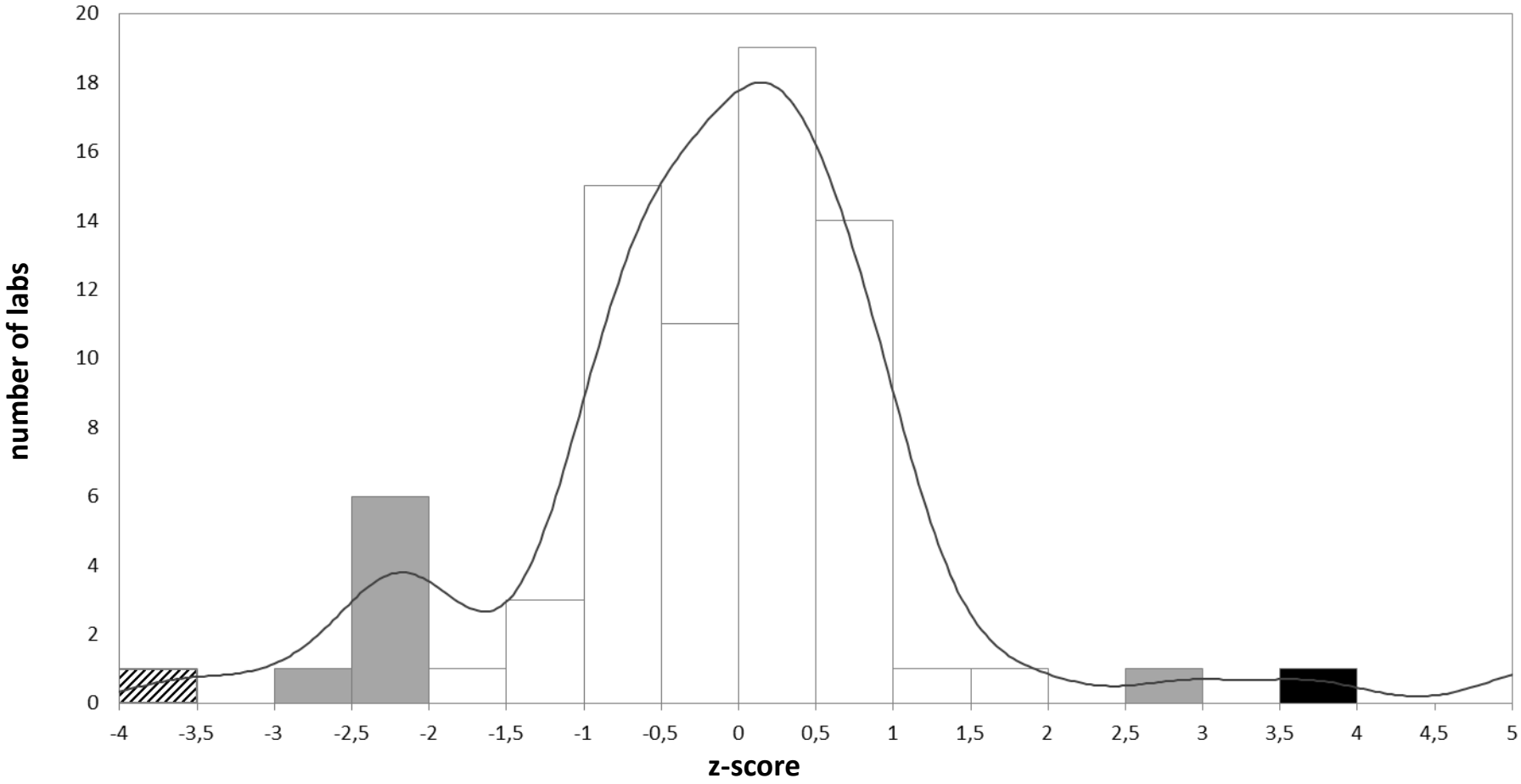
Cyromazine

Results	79
False Neg.	1
AV	0.097 [mg/kg]
CV*	23.5 %
MRRL	0.01 [mg/kg]



Cyromazine

Results	79
False Neg.	1
AV	0.097 [mg/kg]
CV*	23.5 %
MRRL	0.01 [mg/kg]



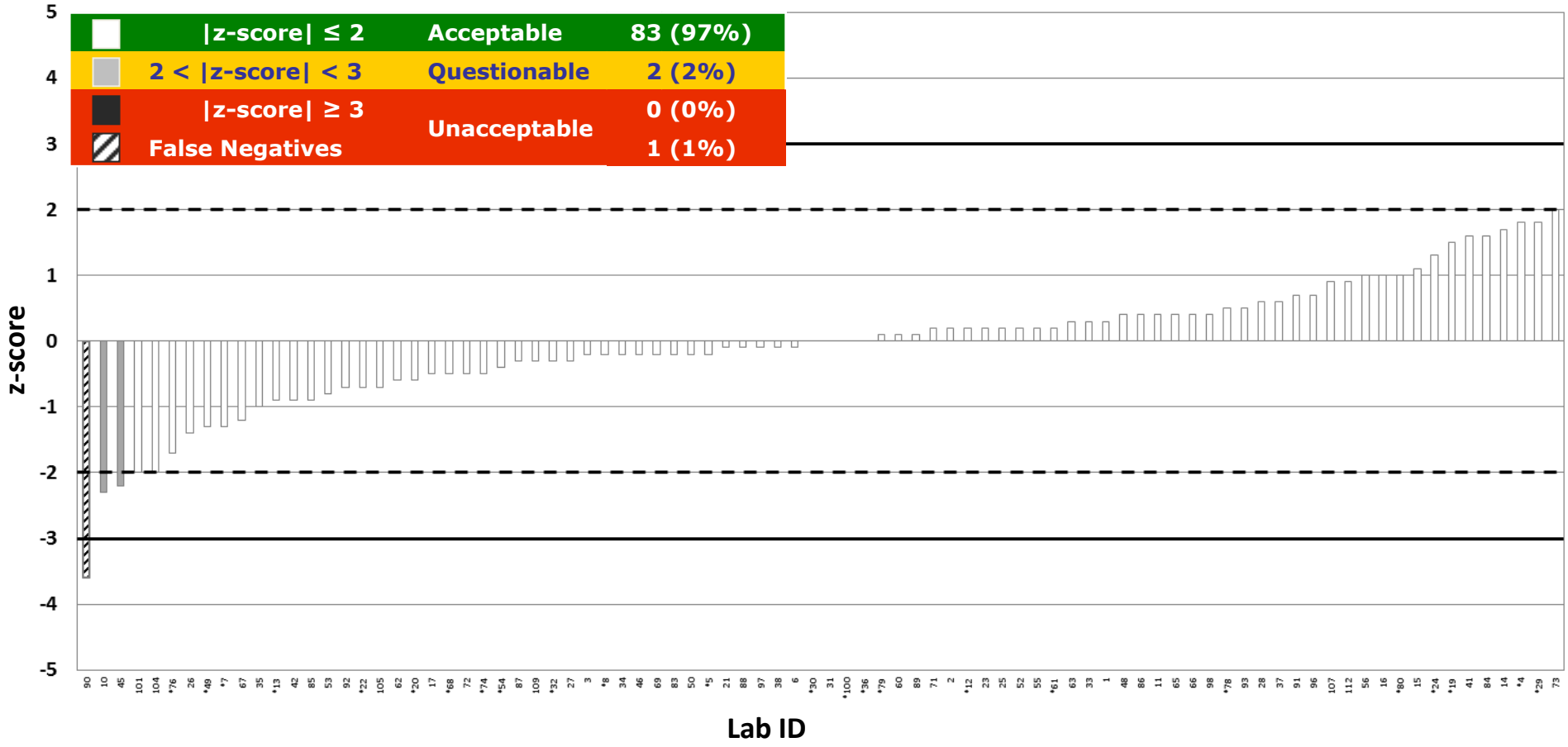
EURL-SRM

FLUAZIFOP (FREE ACID)

Fluazifop (free acid)

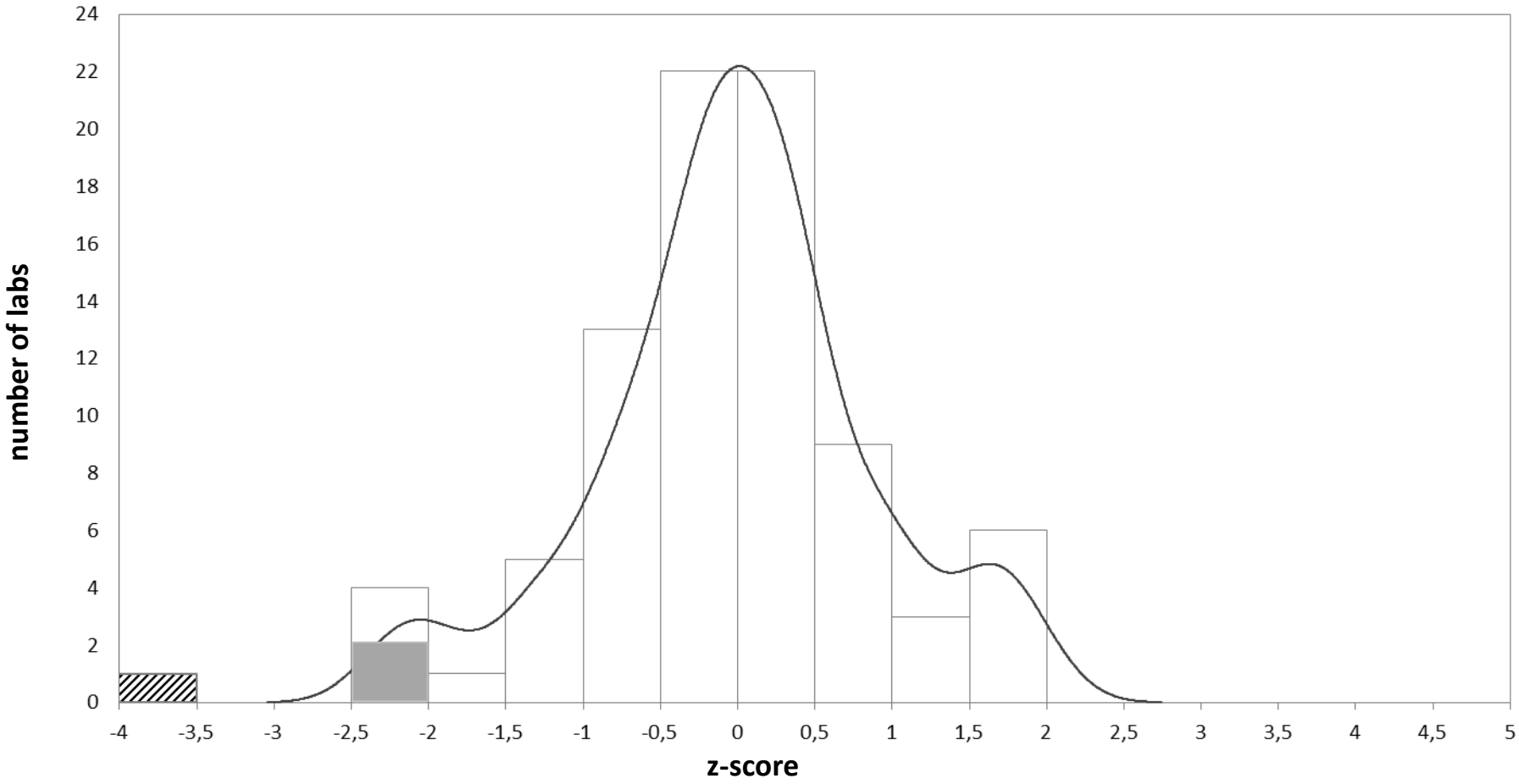
Results	86
False Neg.	1
AV	0.049 [mg/kg]
CV*	20.3 %
MRRL	0.01 [mg/kg]

|z-score| ≤ 2	Acceptable	83 (97%)
2 < |z-score| < 3	Questionable	2 (2%)
|z-score| ≥ 3	Unacceptable	0 (0%)
False Negatives		1 (1%)



Fluazifop (free acid)

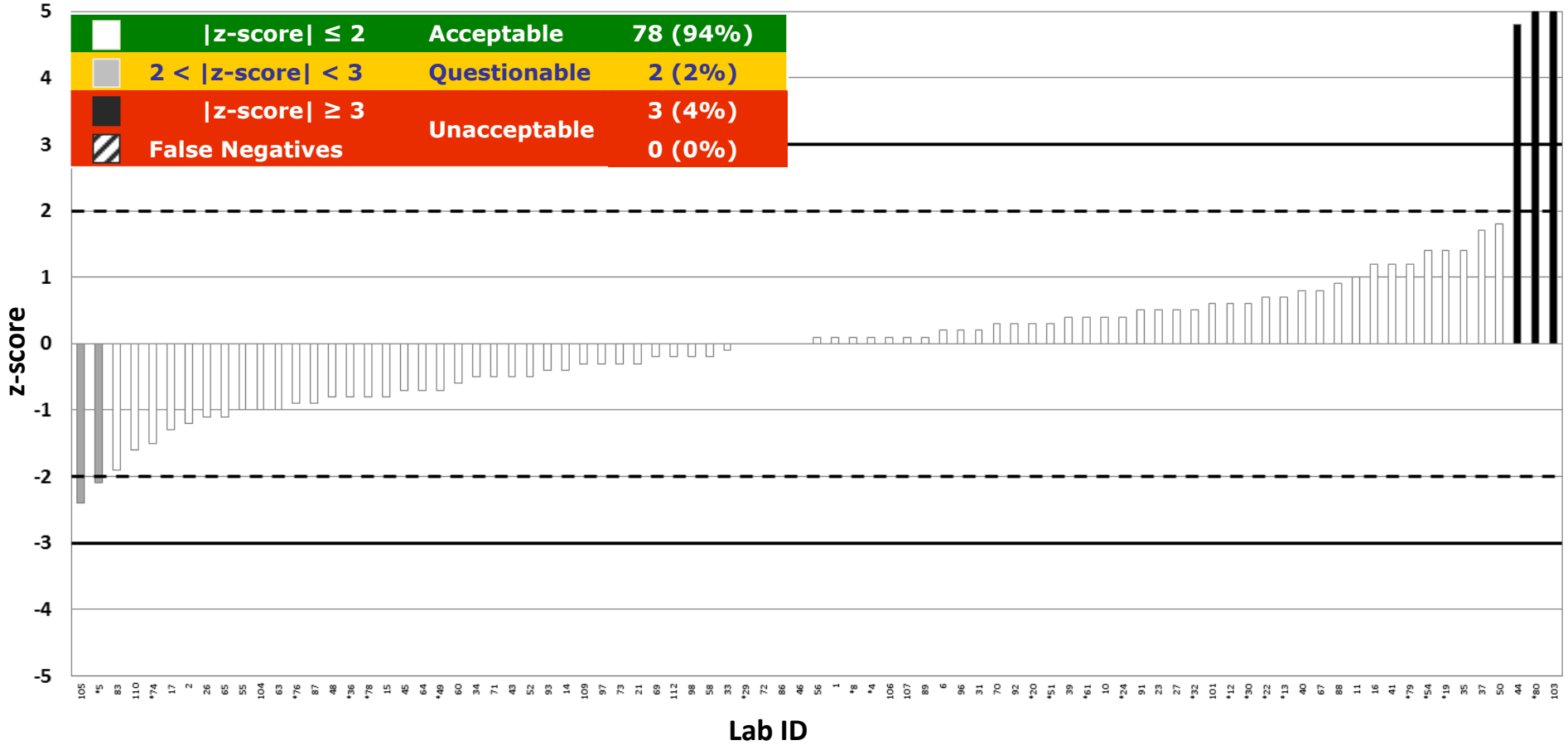
Results	86
False Neg.	1
AV	0.049 [mg/kg]
CV*	20.3 %
MRRL	0.01 [mg/kg]



GLYPHOSATE (PARENT ONLY)

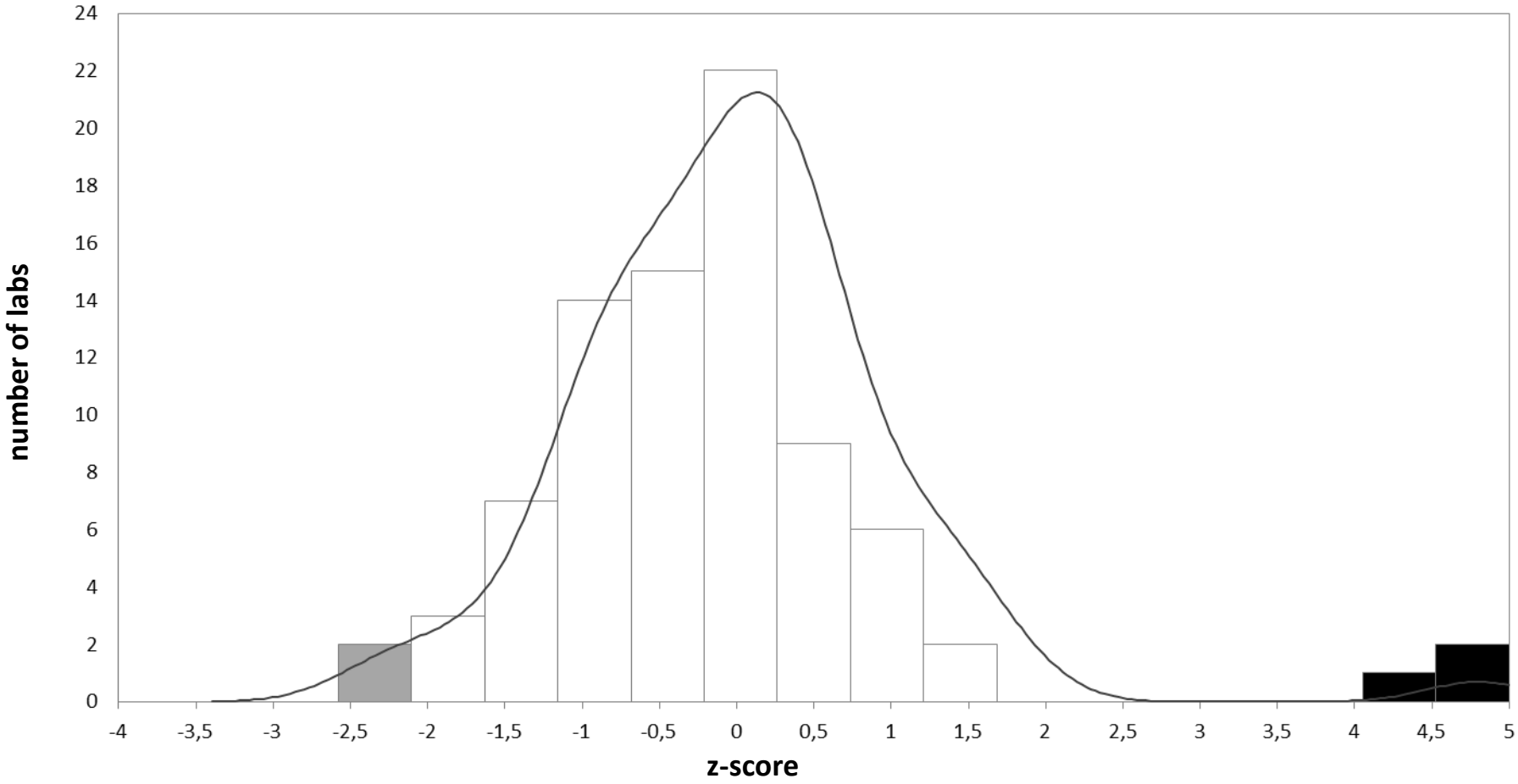
Glyphosate (parent only)

Results	83
False Neg.	0
AV	0.903 [mg/kg]
CV*	22.6 %
MRRL	0.03 [mg/kg]



Glyphosate (parent only)

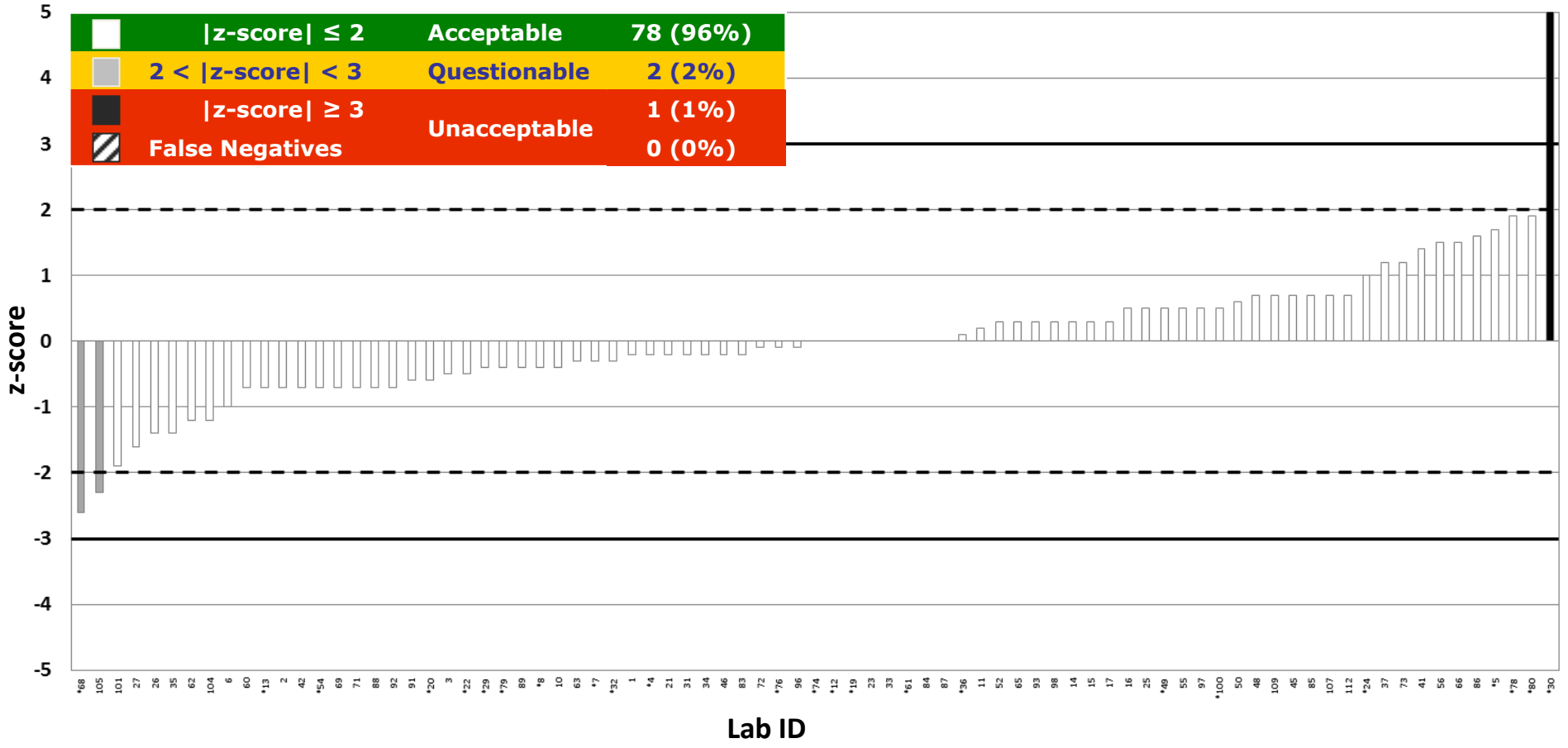
Results	83
False Neg.	0
AV	0.903 [mg/kg]
CV*	22.6 %
MRRL	0.03 [mg/kg]



HALOXYFOP (FREE ACID)

Haloxyfop (free acid)

Results	81
False Neg.	0
AV	0.017 [mg/kg]
CV*	20.4 %
MRRL	0.003 [mg/kg]

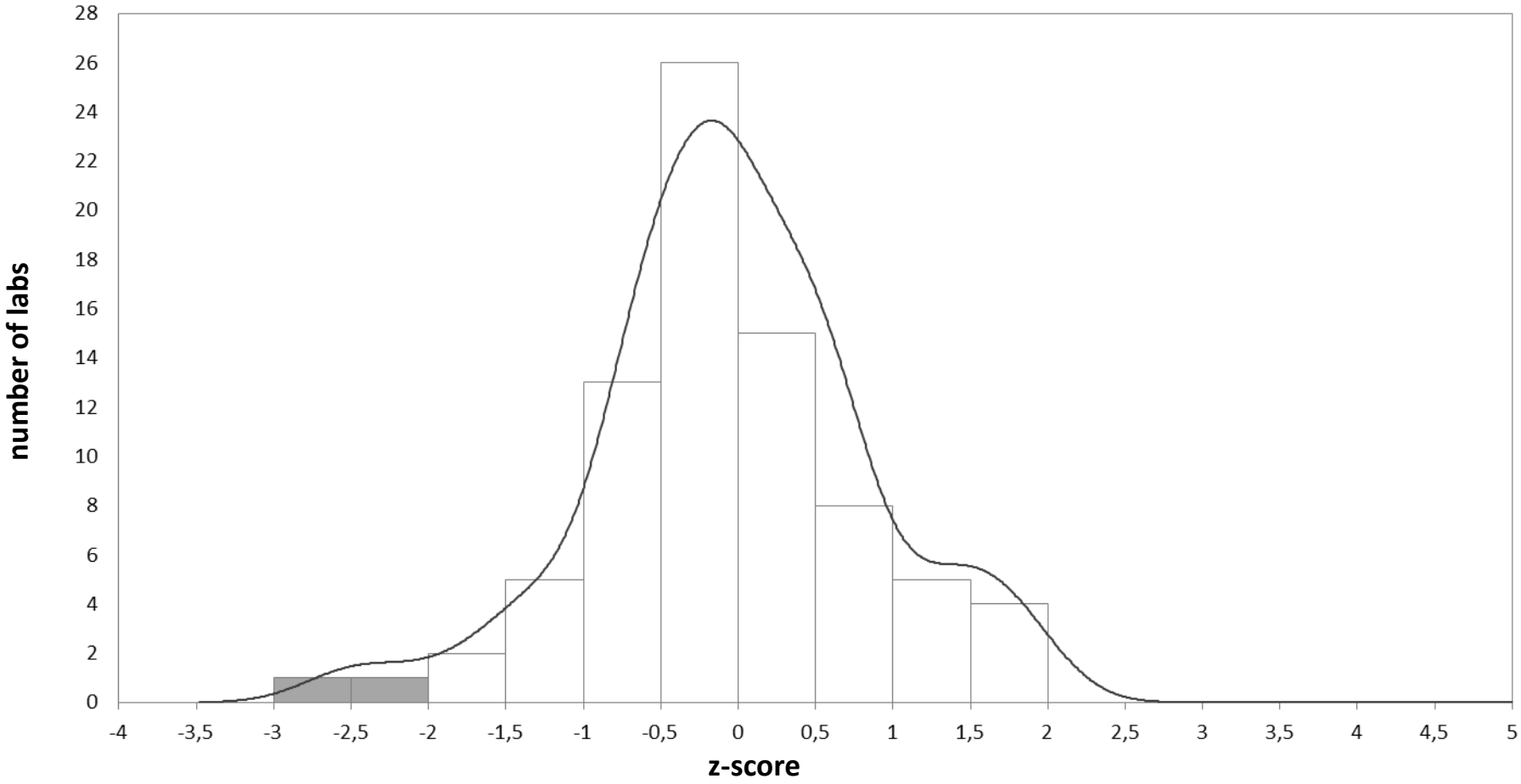


EURL-SRM

HALOXYFOP (FREE ACID)

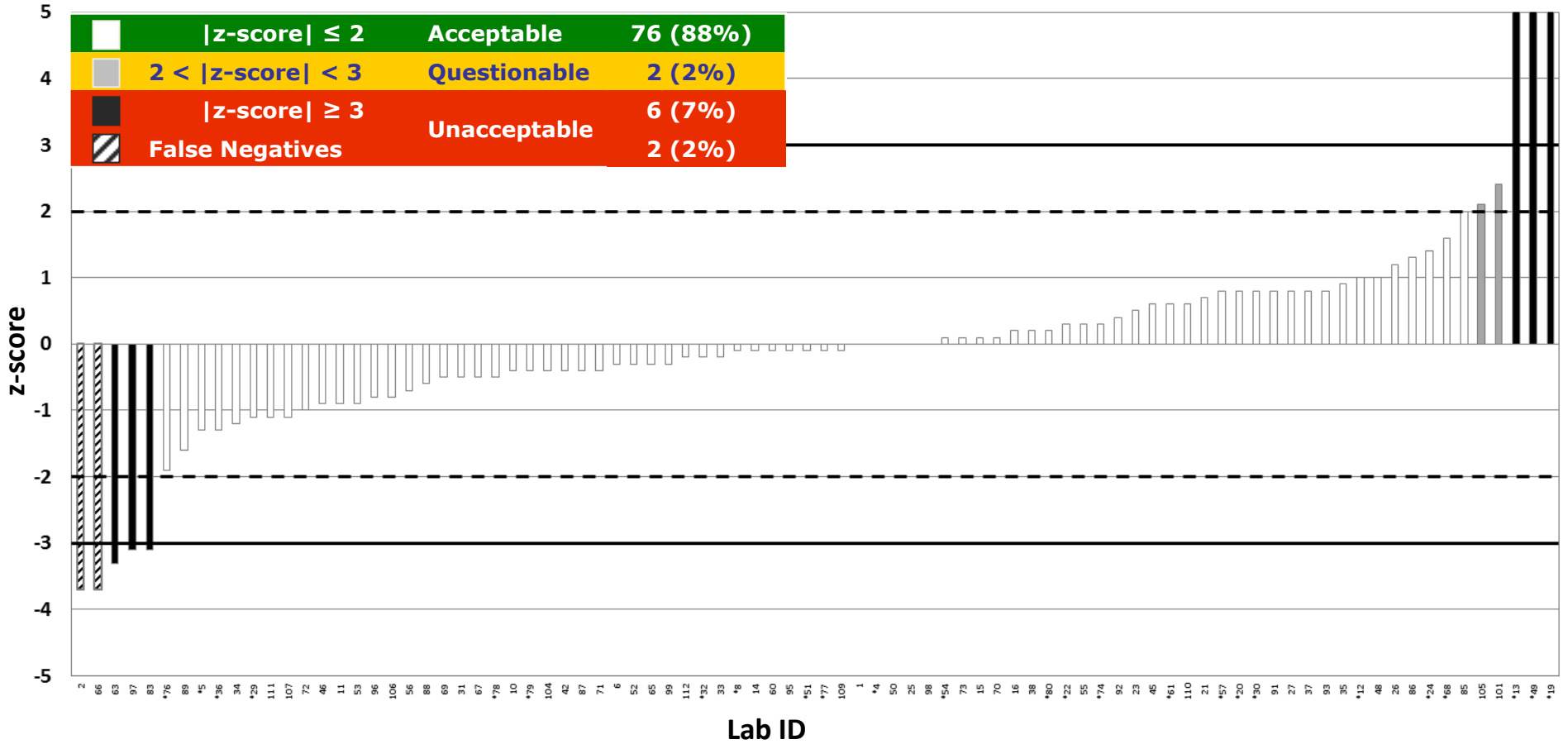
Haloxyfop (free acid)

Results	81
False Neg.	0
AV	0.017 [mg/kg]
CV*	20.4 %
MRRL	0.003 [mg/kg]



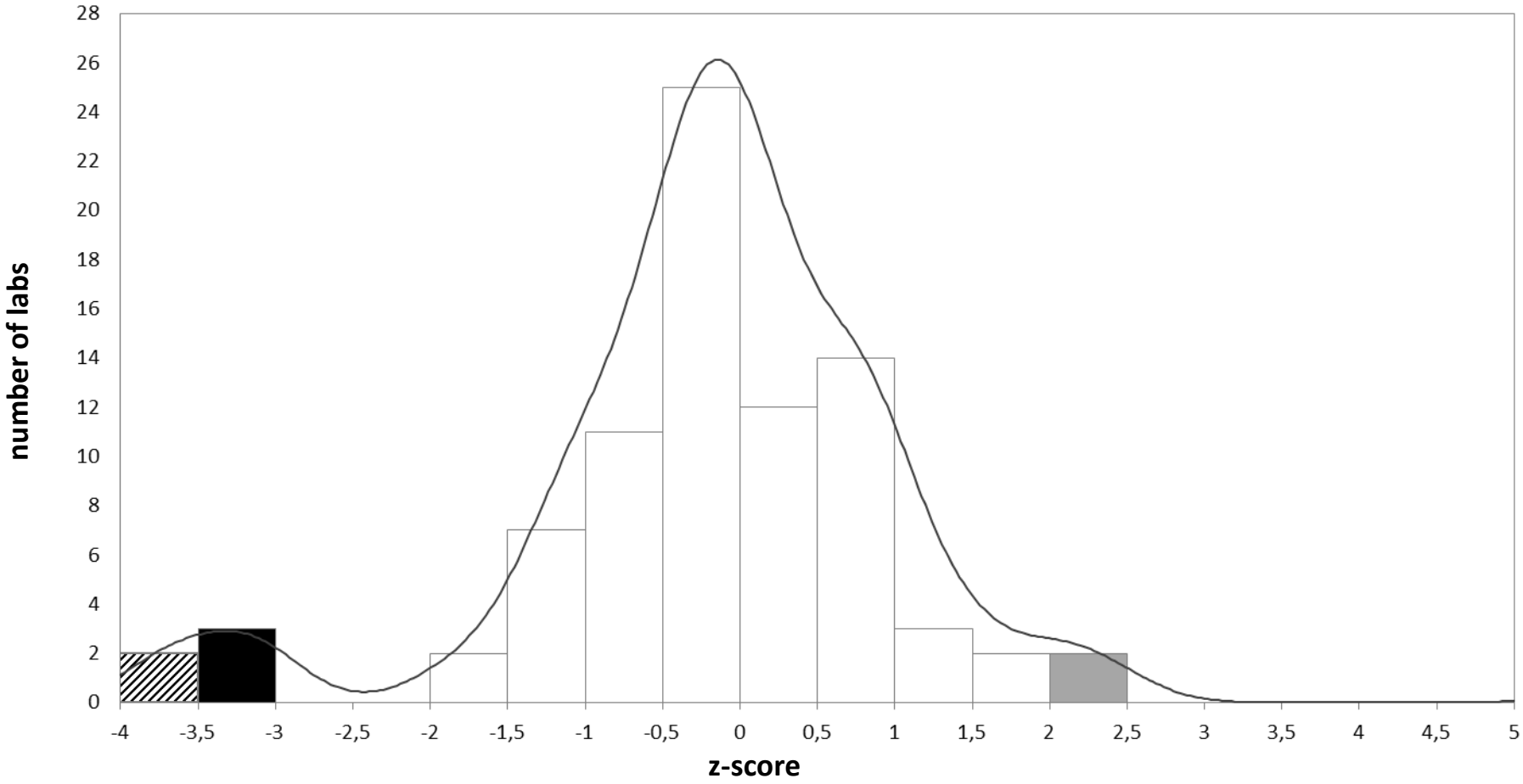
Mepiquat chloride

Results	86
False Neg.	2
AV	0.12 [mg/kg]
CV*	22.9 %
MRRL	0.01 [mg/kg]



Mepiquat chloride

Results	86
False Neg.	2
AV	0.12 [mg/kg]
CV*	22.9 %
MRRL	0.01 [mg/kg]

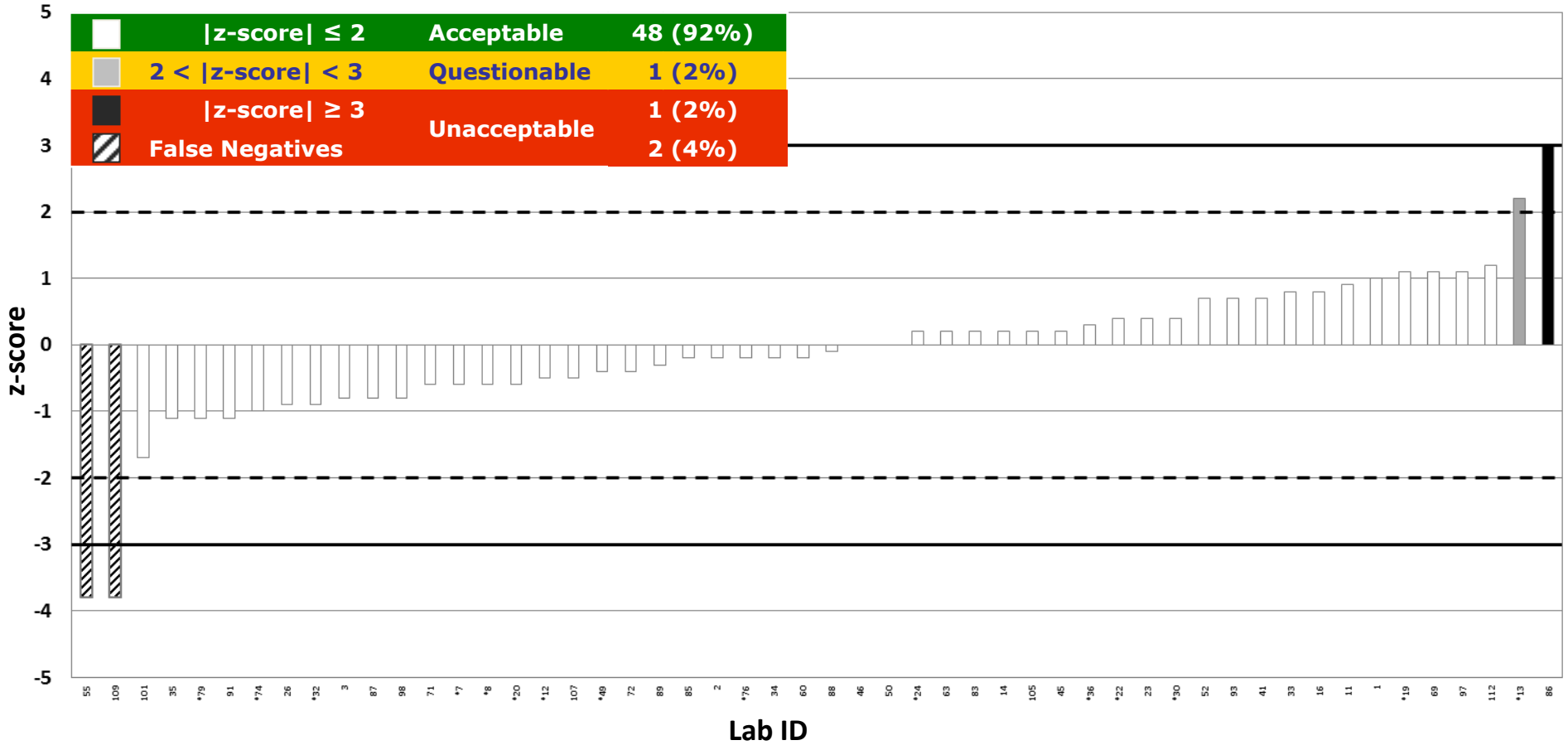


EURL-SRM

2.4-DB (FREE ACID)

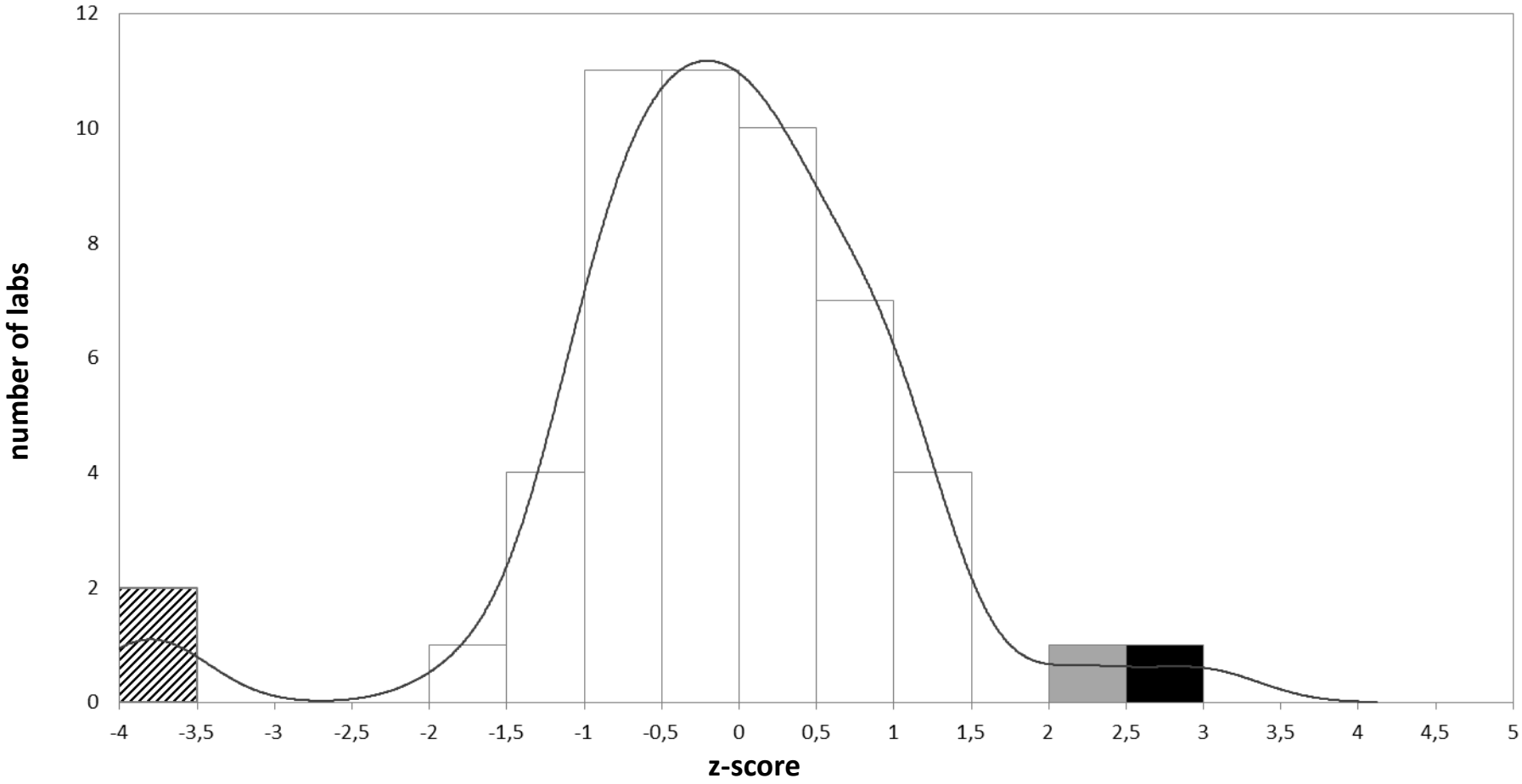
2.4-DB (free acid)

Results	52
False Neg.	2
AV	0.18 [mg/kg]
CV*	20.7 %
MRRL	0.01 [mg/kg]



2.4-DB (free acid)

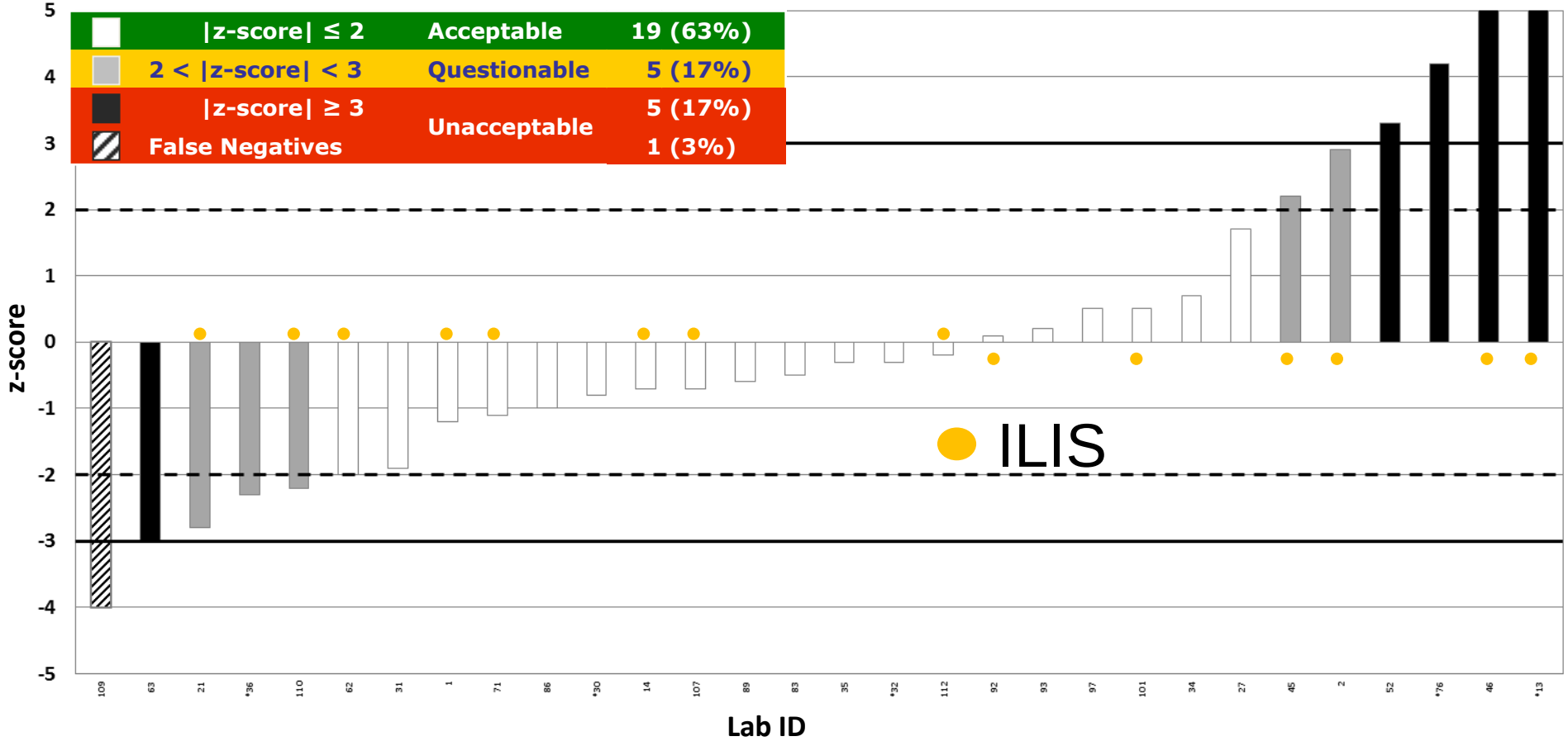
Results	52
False Neg.	2
AV	0.18 [mg/kg]
CV*	20.7 %
MRRL	0.01 [mg/kg]



DIQUAT (DICATION)

Diquat (dication)

Results	30
False Neg.	1
AV	1.7 [mg/kg]
CV*	52.8 %
MRRL	0.02 [mg/kg]

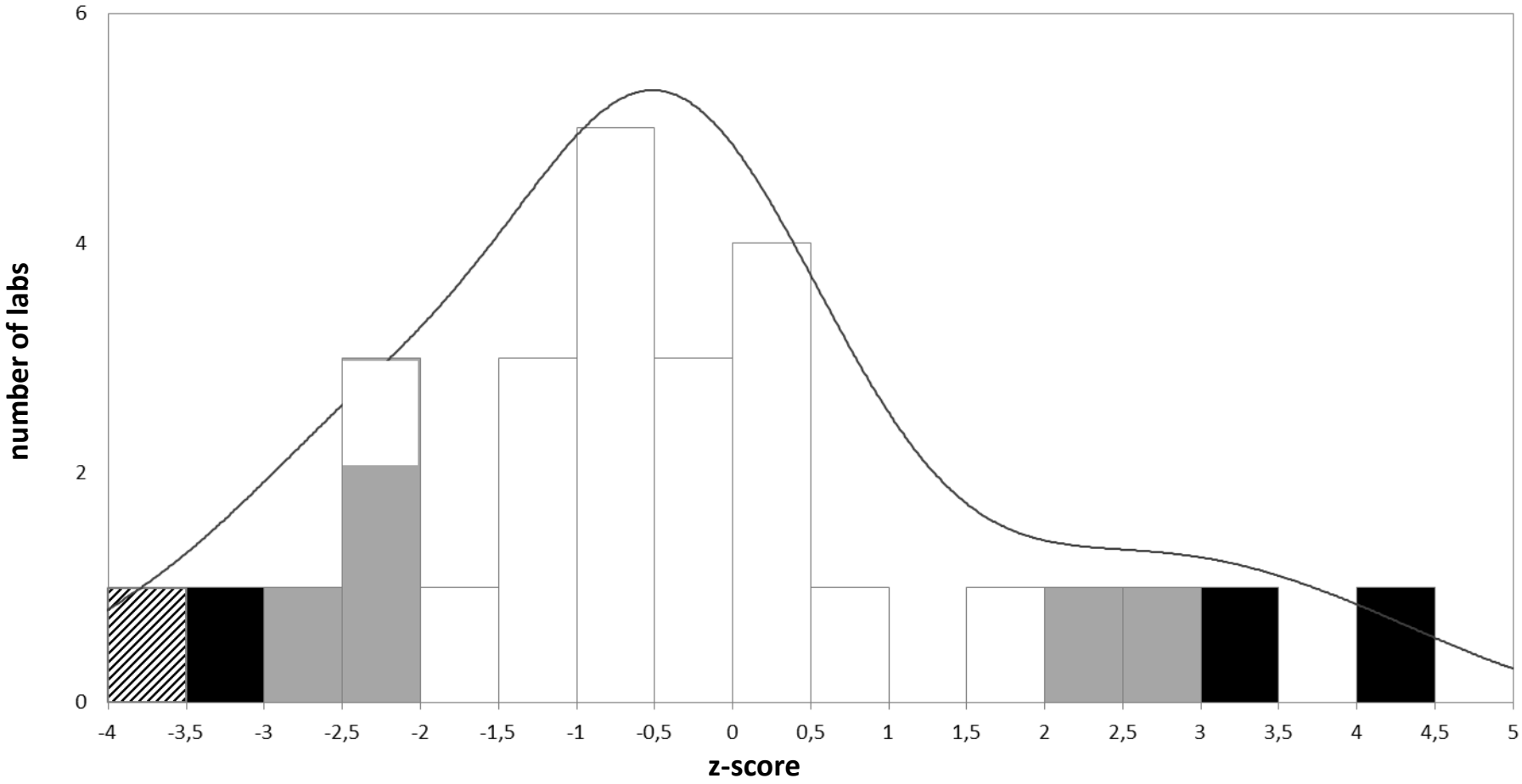


EURL-SRM

DIQUAT (DICATION)

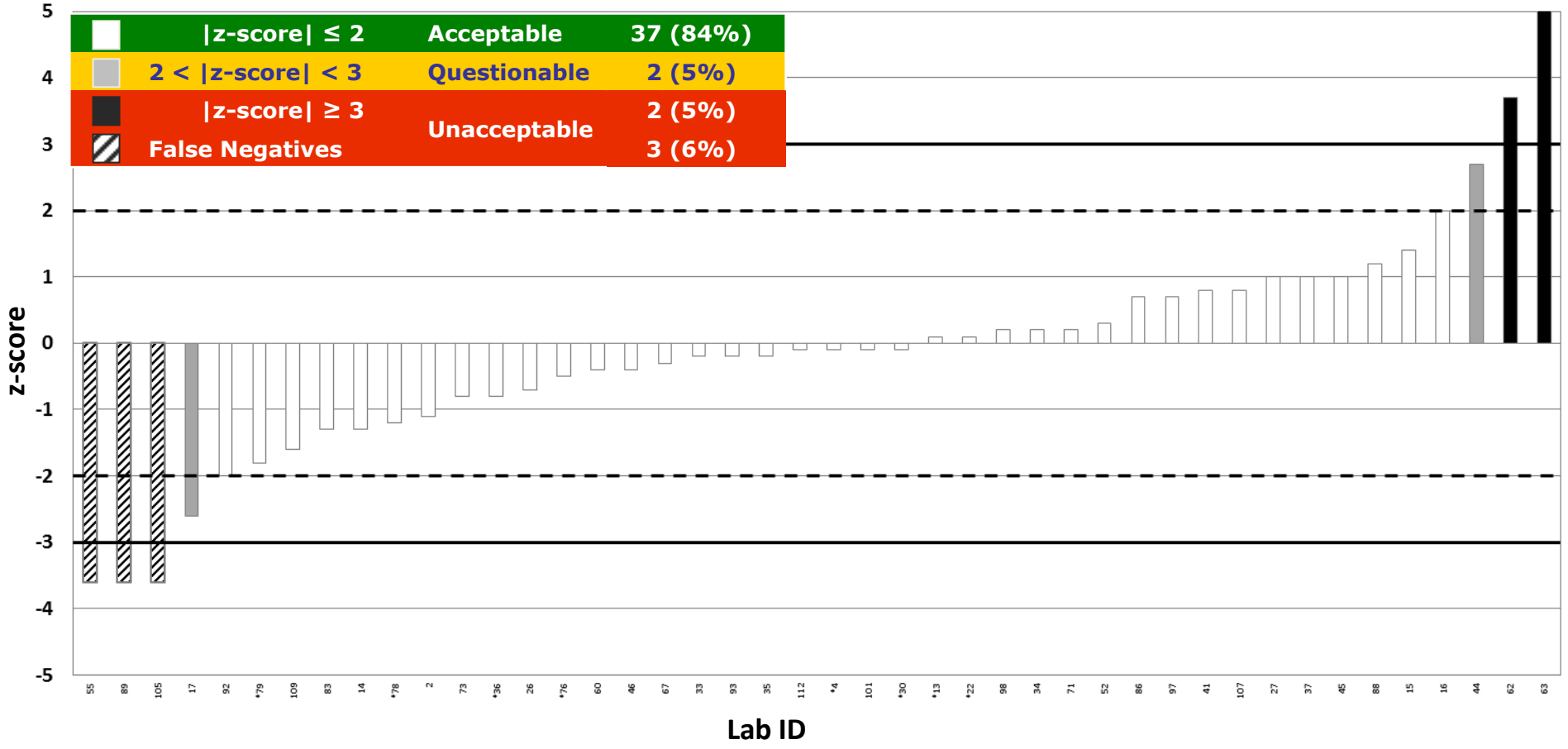
Diquat (dication)

Results	30
False Neg.	1
AV	1.7 [mg/kg]
CV*	52.8 %
MRRL	0.02 [mg/kg]



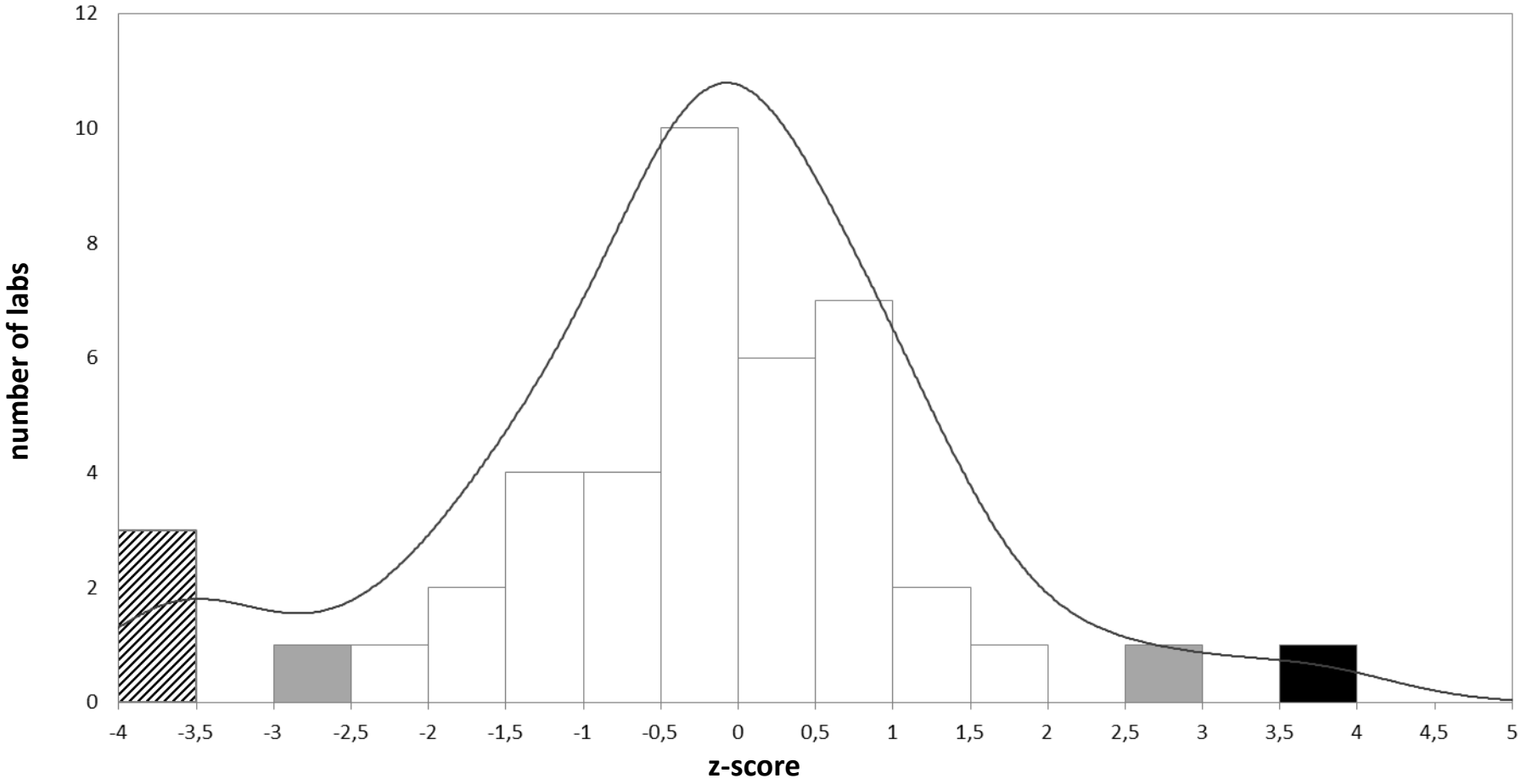
Glufosinate

Results	44
False Neg.	3
AV	0.20 [mg/kg]
CV*	28.7 %
MRRL	0.02



Glufosinate

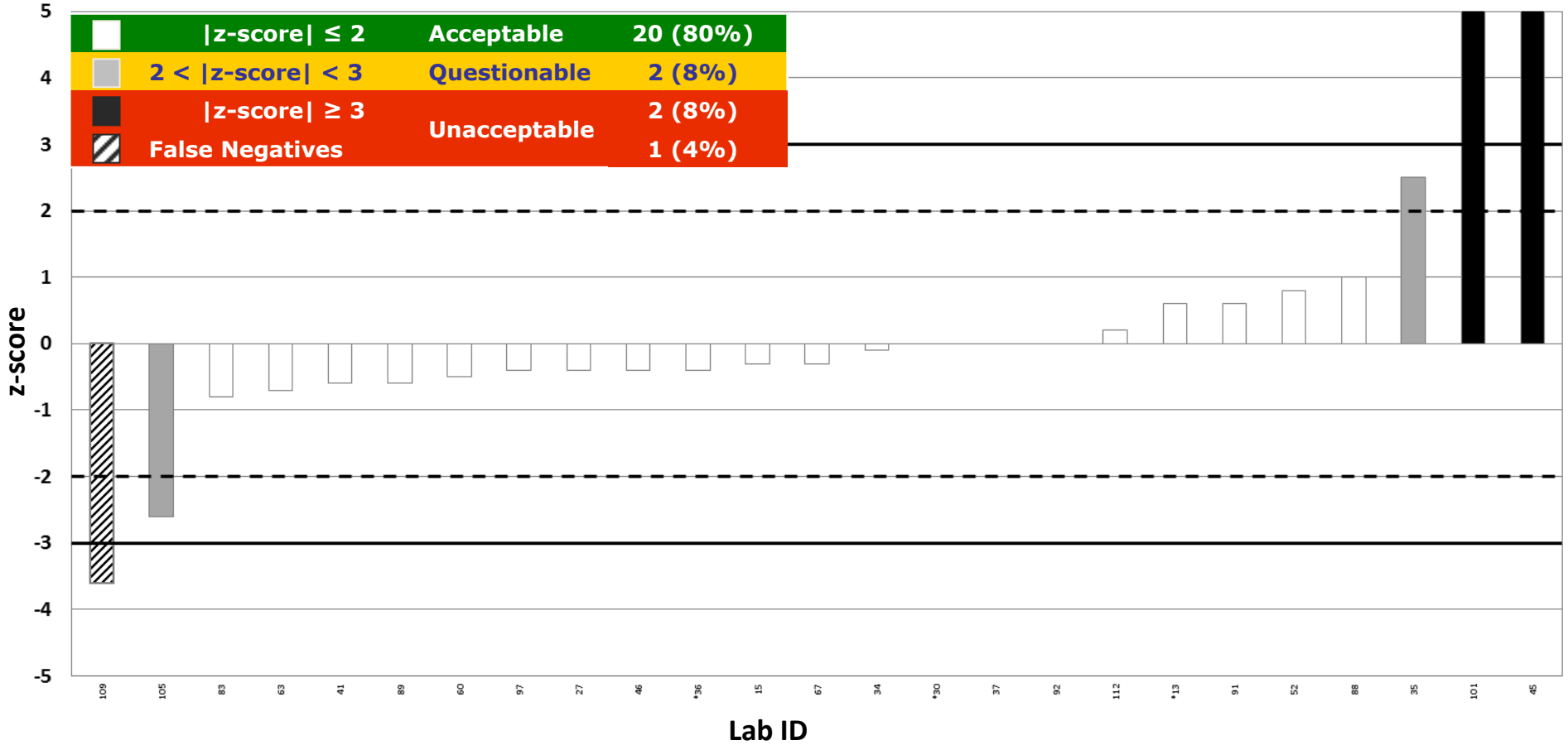
Results	44
False Neg.	3
AV	0.20 [mg/kg]
CV*	28.7 %
MRRL	0.02



MPP (METABOLITE OF GLUFOSINATE)

MPP (metabolite of glufosinate)

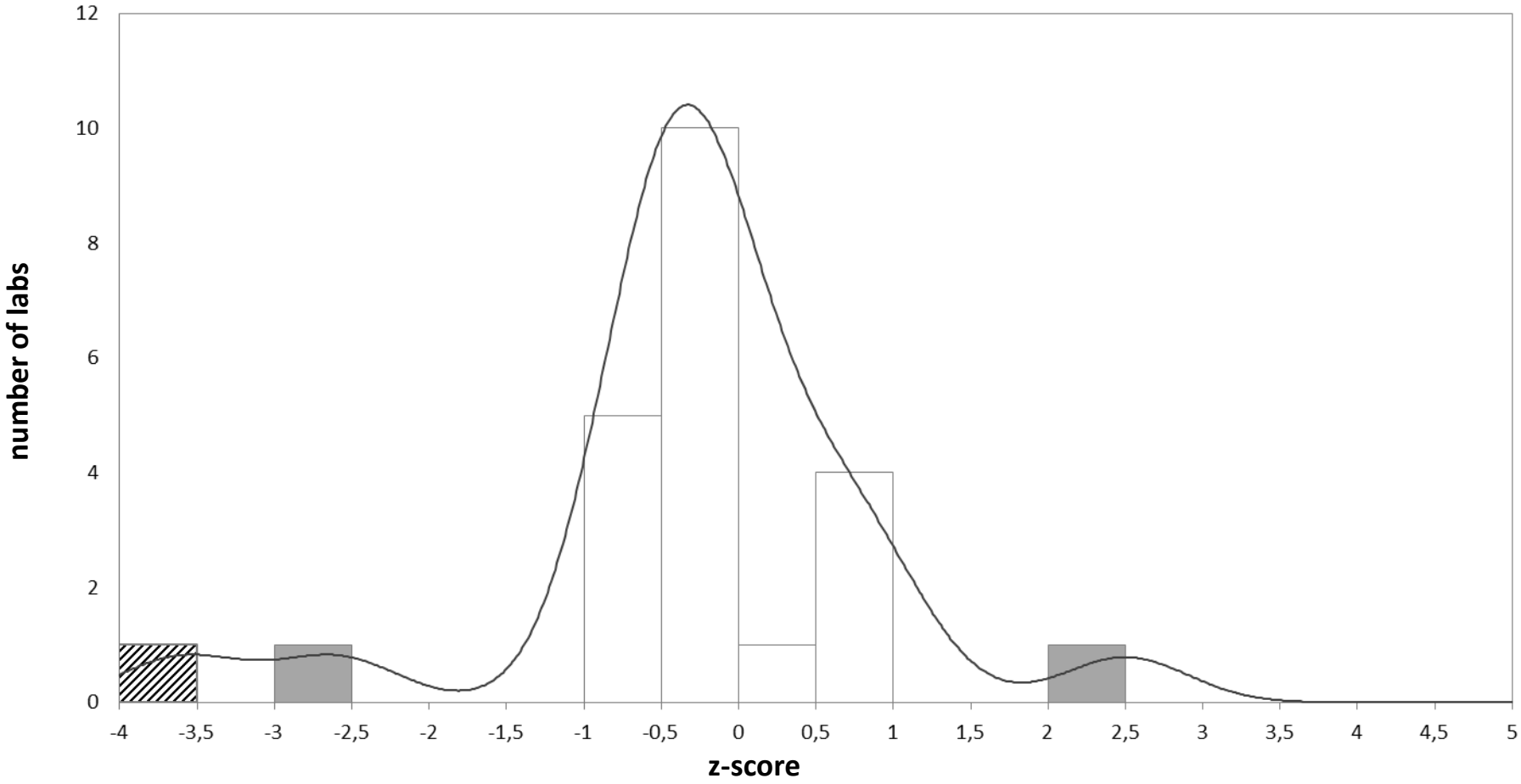
Results	25
False Neg.	1
AV	0.19 [mg/kg]
CV*	18.9 %
MRRL	0.02



MPP (METABOLITE OF GLUFOSINATE)

MPP (metabolite of glufosinate)

Results	25
False Neg.	1
AV	0.19 [mg/kg]
CV*	18.9 %
MRRL	0.02

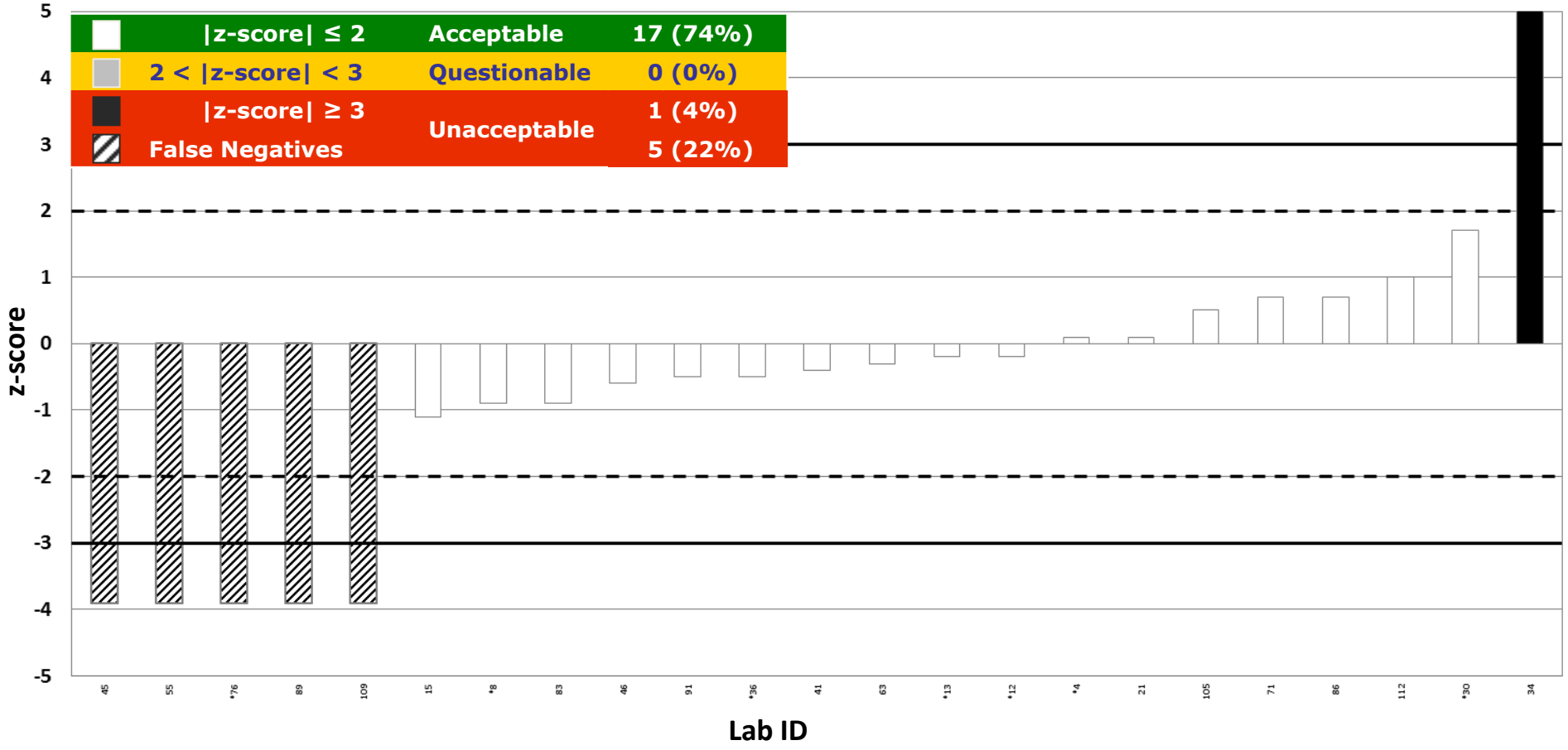


EURL-SRM

N-ACETYL-GLYPHOSATE

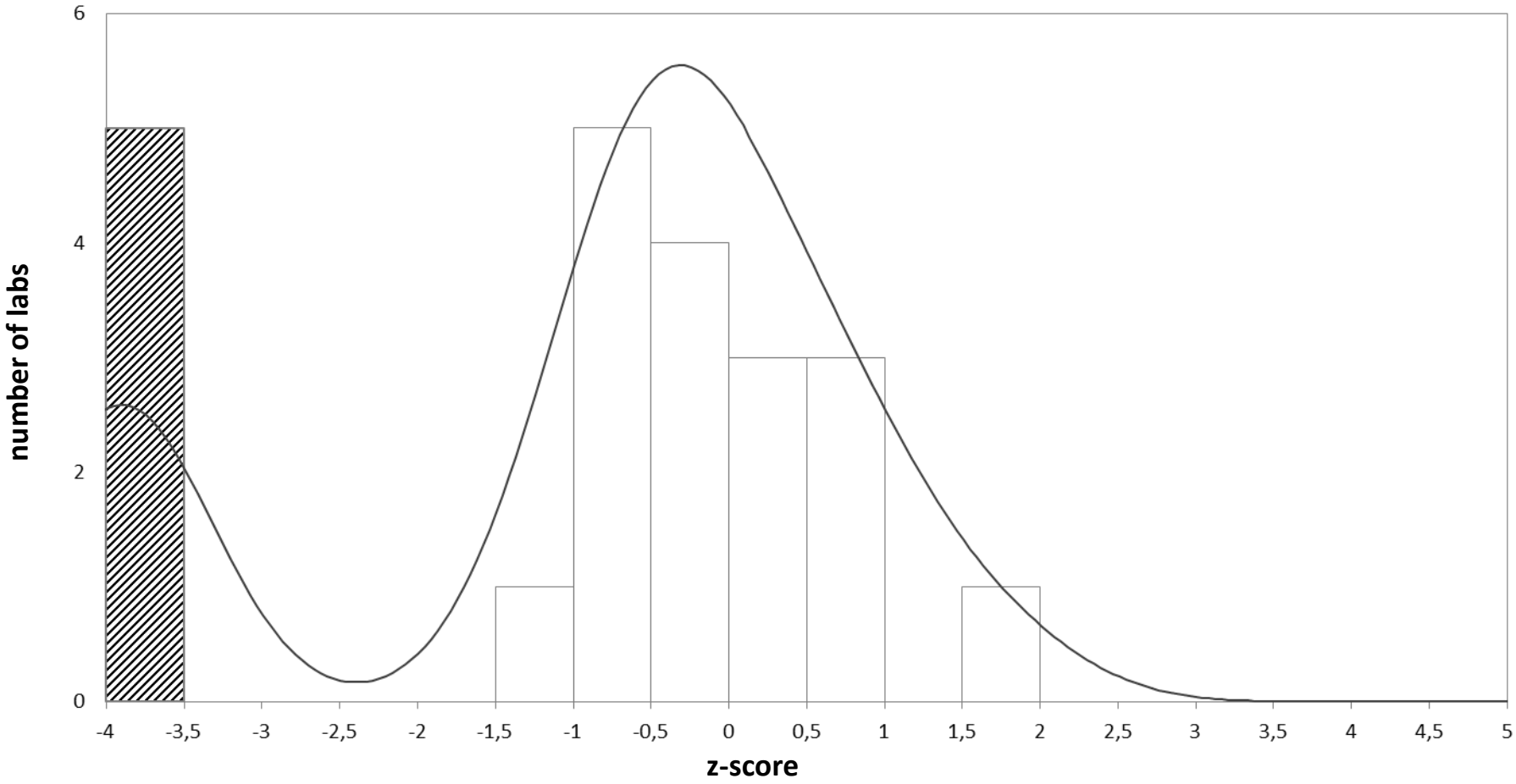
N-Acetyl-Glyphosate

Results	23
False Neg.	5
AV	0.84 [mg/kg]
CV*	21.1 %
MRRL	0.02



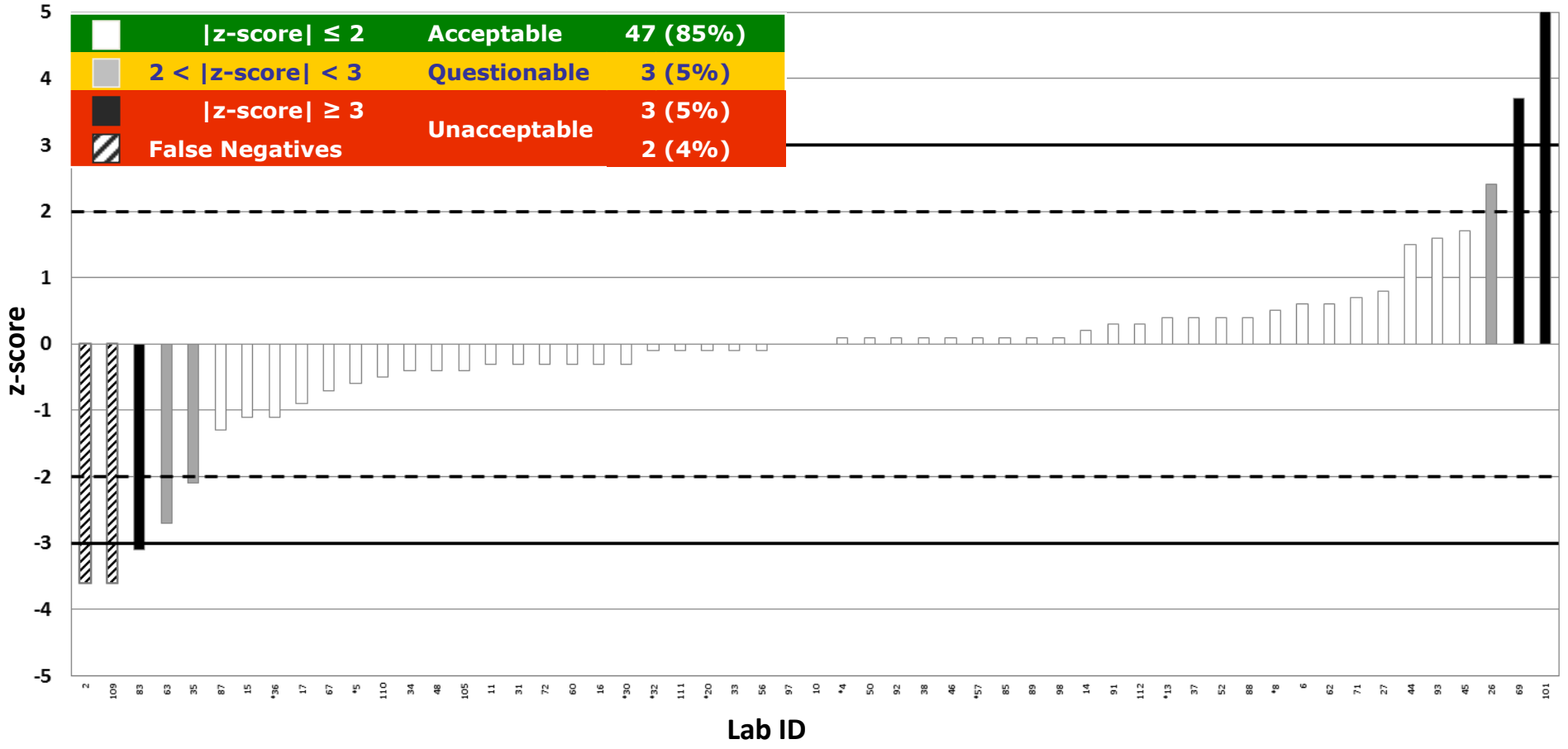
N-Acetyl-Glyphosate

Results	23
False Neg.	5
AV	0.84 [mg/kg]
CV*	21.1 %
MRRL	0.02



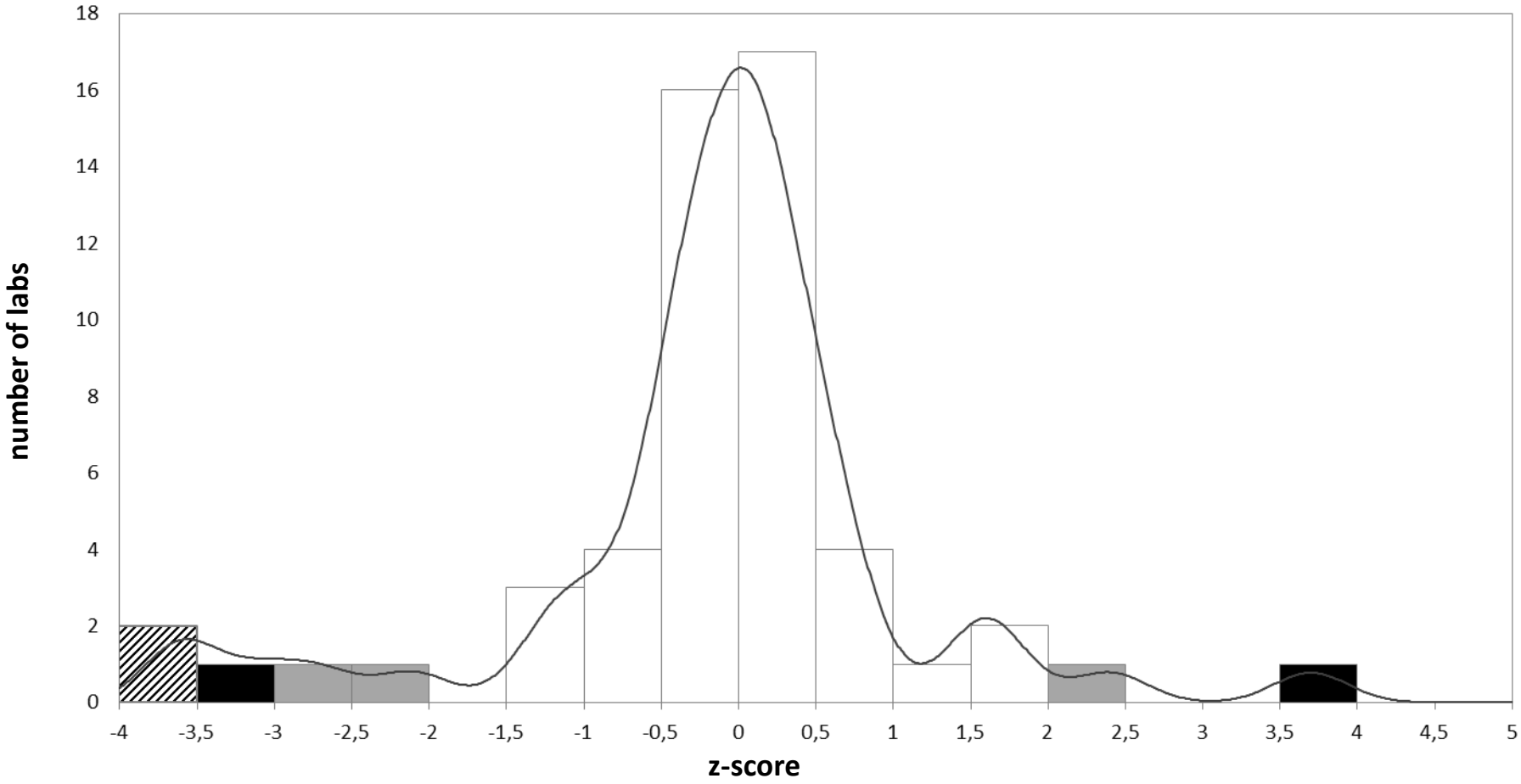
Perchlorate (anion)

Results	55
False Neg.	2
AV	0.10 [mg/kg]
CV*	16.9 %
MRRL	0.01



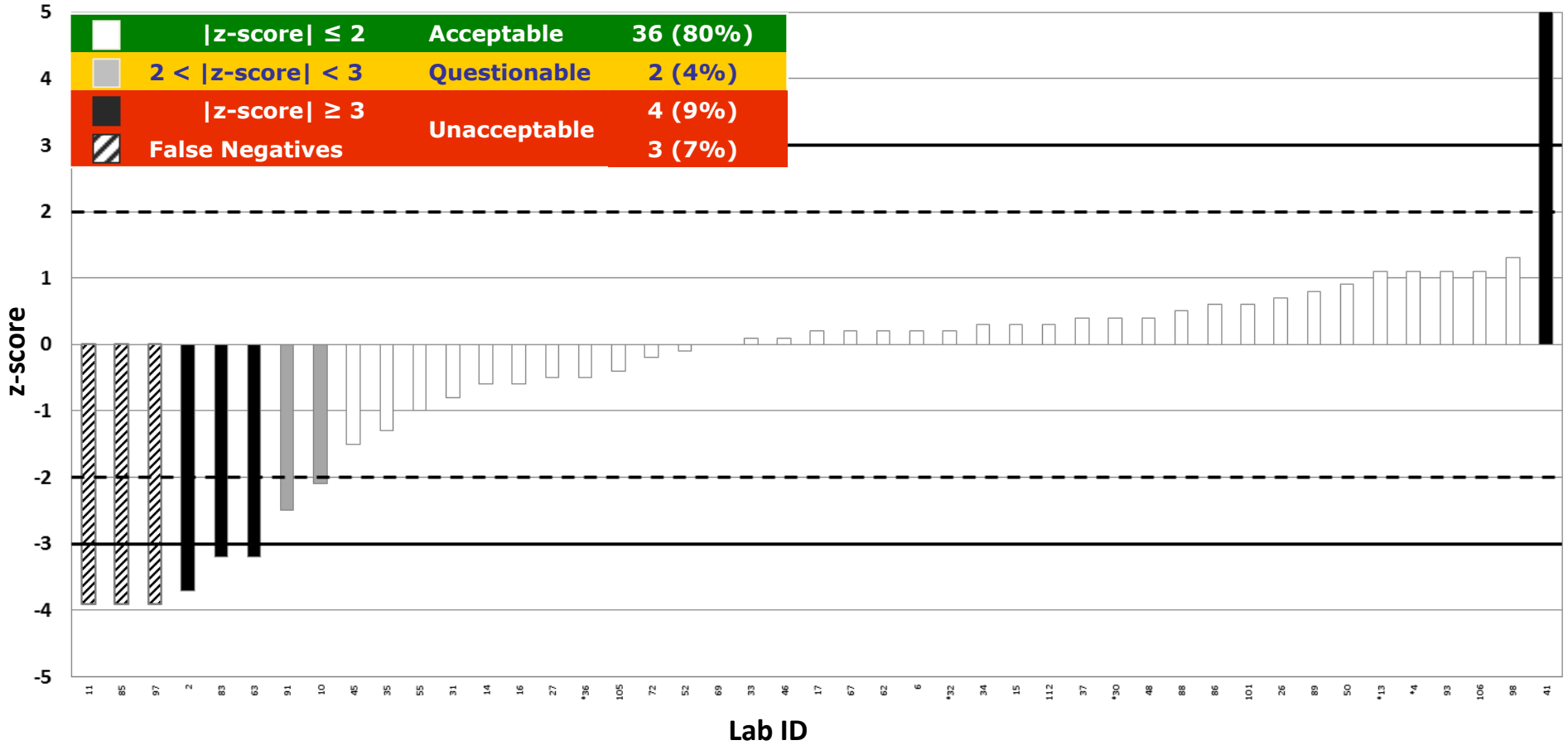
Perchlorate (anion)

Results	55
False Neg.	2
AV	0.10 [mg/kg]
CV*	16.9 %
MRRL	0.01



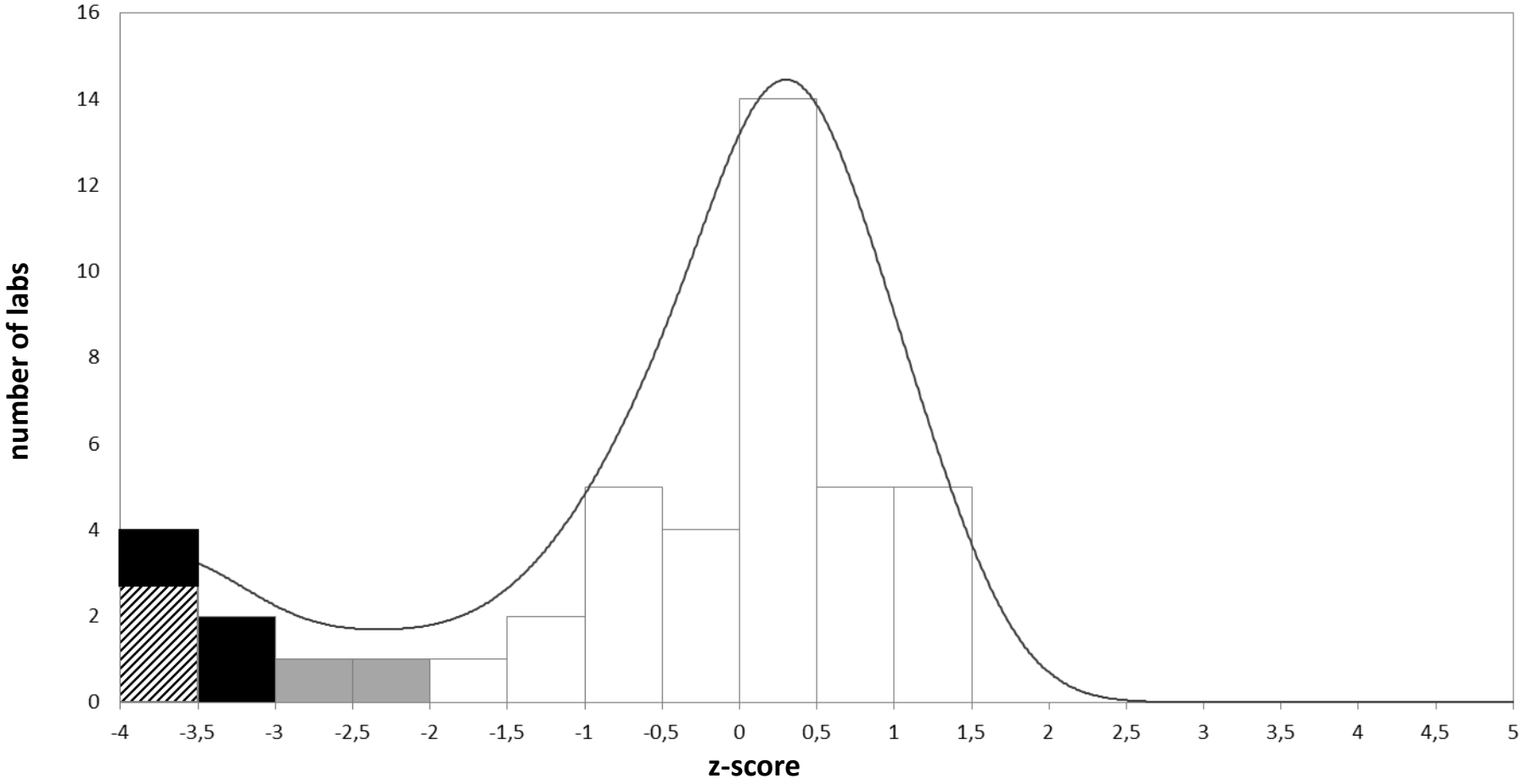
Phosphonic acid

Results	45
False Neg.	3
AV	1.8 [mg/kg]
CV*	24.3 %
MRRL	0.05 [mg/kg]



Phosphonic acid

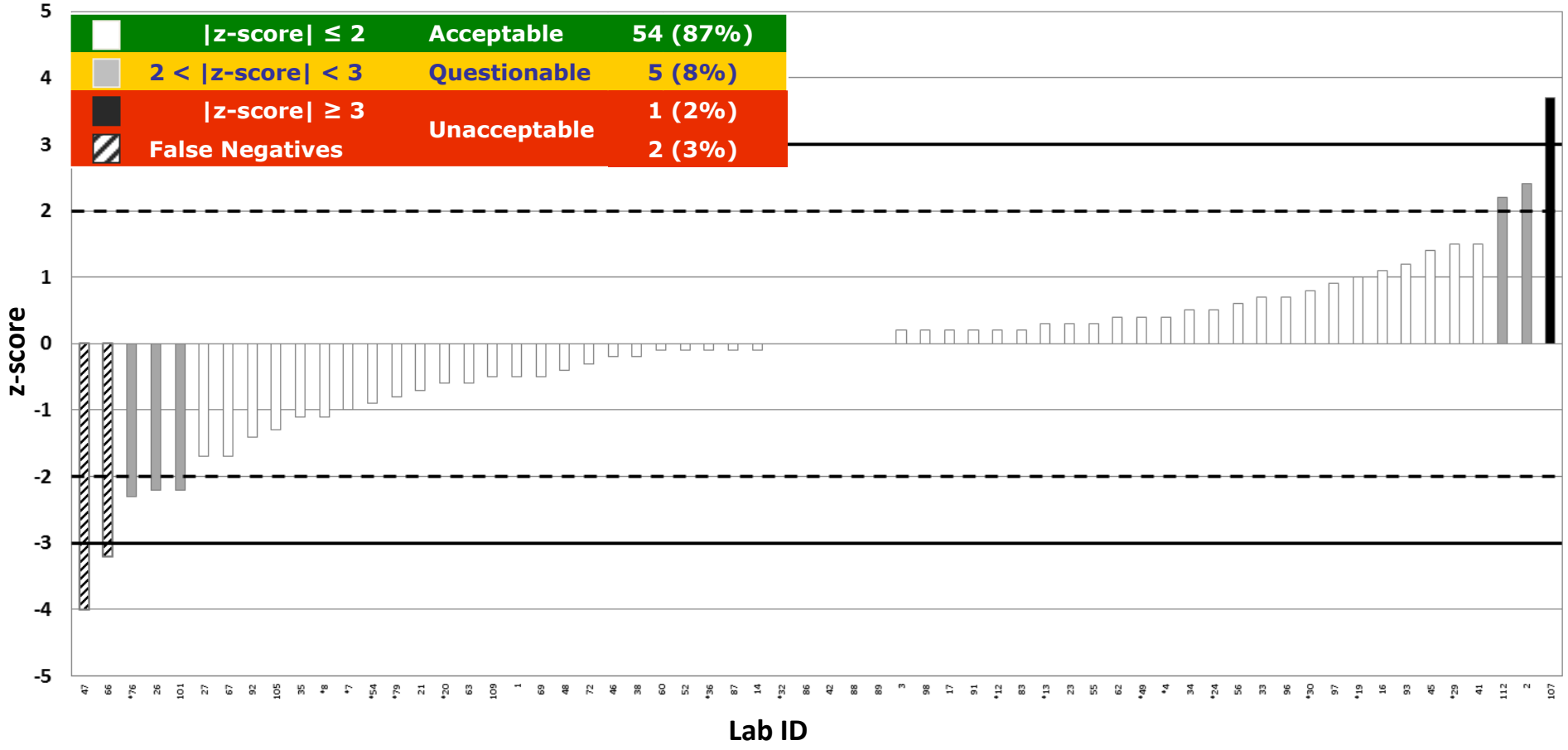
Results	45
False Neg.	3
AV	1.8 [mg/kg]
CV*	24.3 %
MRRL	0.05 [mg/kg]



QUIZALOFOP (FREE ACID)

Quizalofop (free acid)

Results	62
False Neg.	2
AV	0.052 [mg/kg]
CV*	23.6 %
MRRL	0.01 [mg/kg]

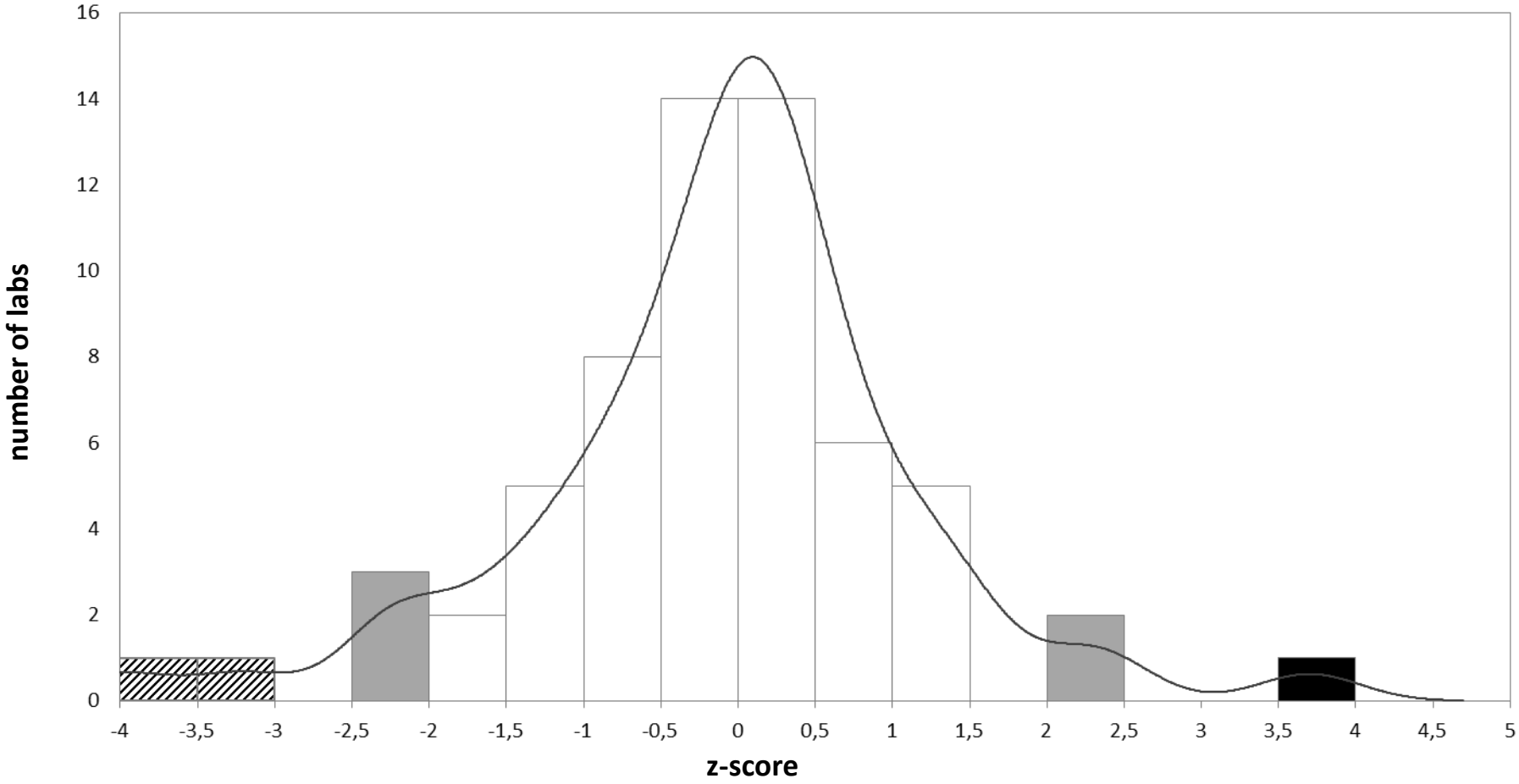


EURL-SRM

QUIZALOFOP (FREE ACID)

Quizalofop (free acid)

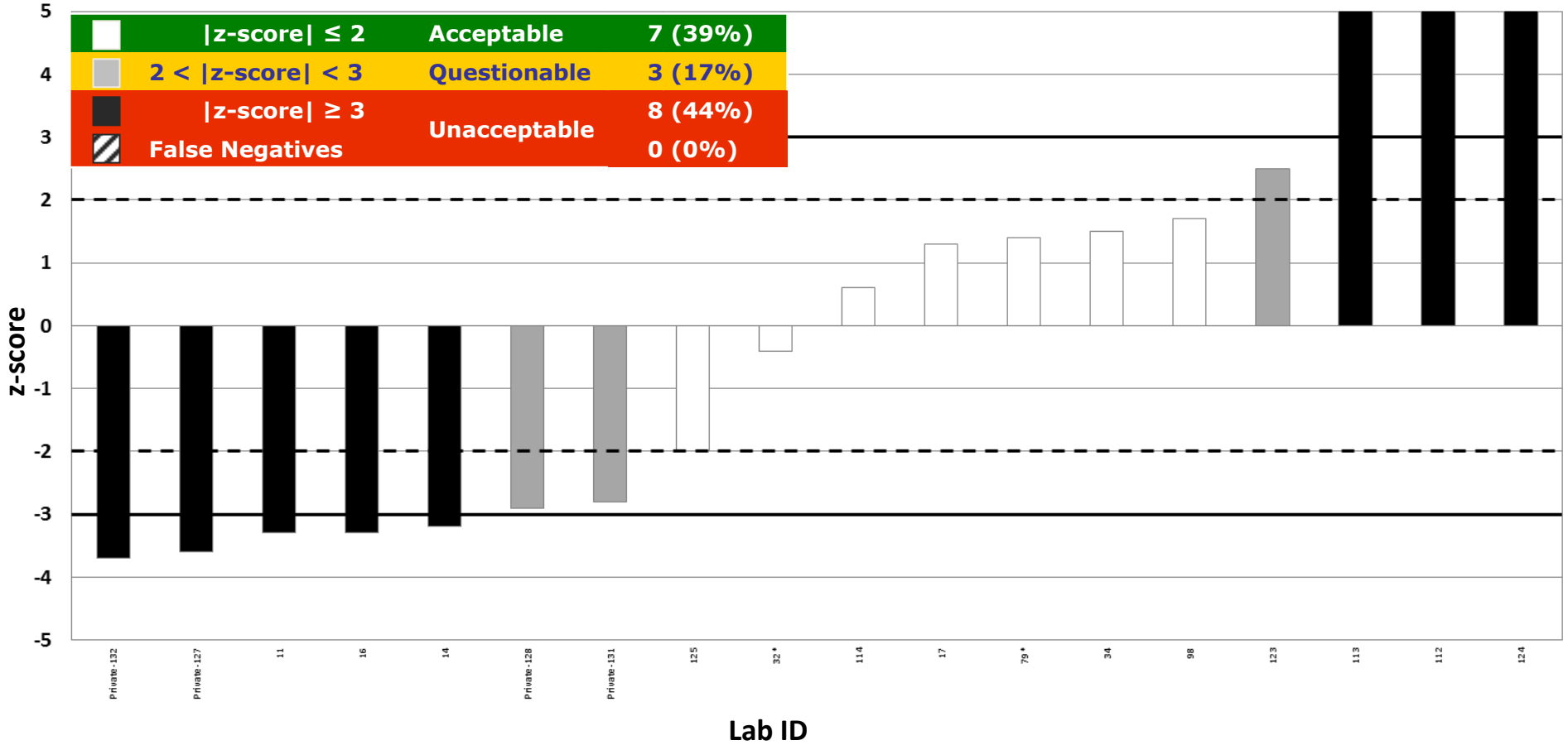
Results	62
False Neg.	2
AV	0.052 [mg/kg]
CV*	23.6 %
MRRL	0.01 [mg/kg]



PHOSPHANE

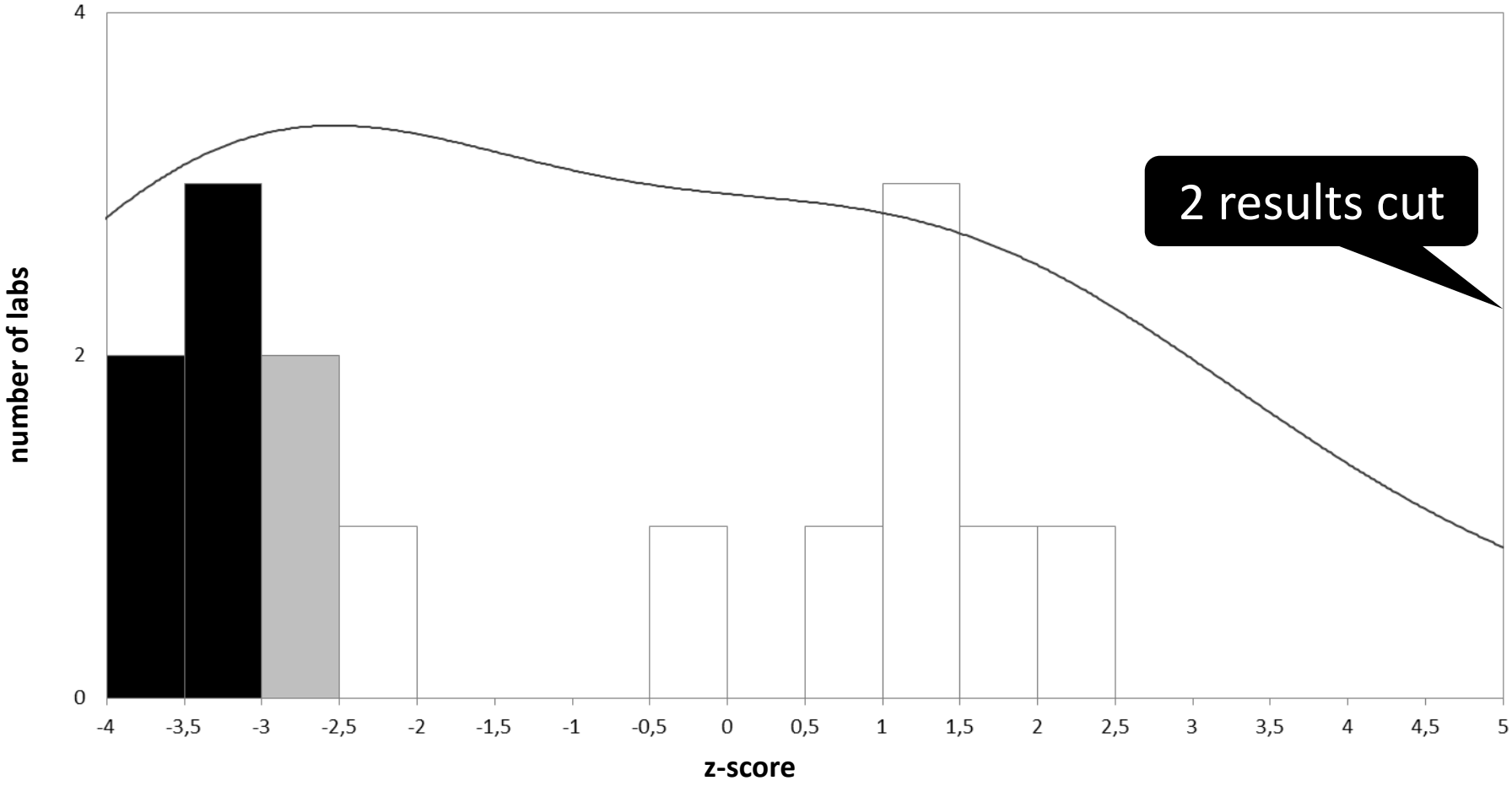
Phosphane I

Results	18
False Neg.	0
AV	*0.092* [mg/kg]
CV*	93.1 %
MRRL	0.005 [mg/kg]



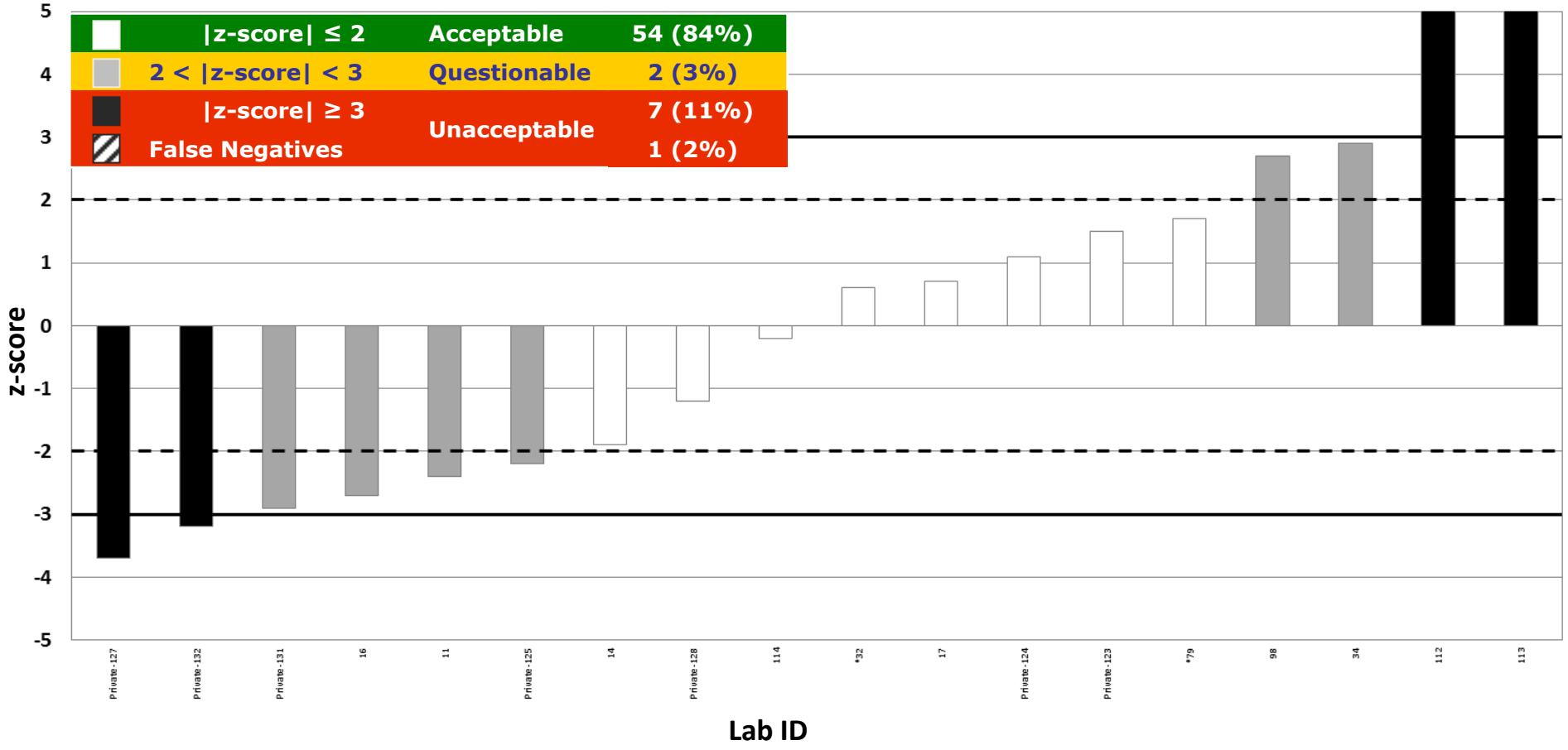
Phosphane I

Results	**18**
False Neg.	**0**
AV	*0.092* **[mg/kg]**
CV*	**93.1 %**
MRRL	**0.005 [mg/kg]**



Phosphane II („PH_3 sample“)

Results	18
False Neg.	
AV	*0.040* [mg/kg]
CV*	74.8 %
MRRL	0.005 [mg/kg]

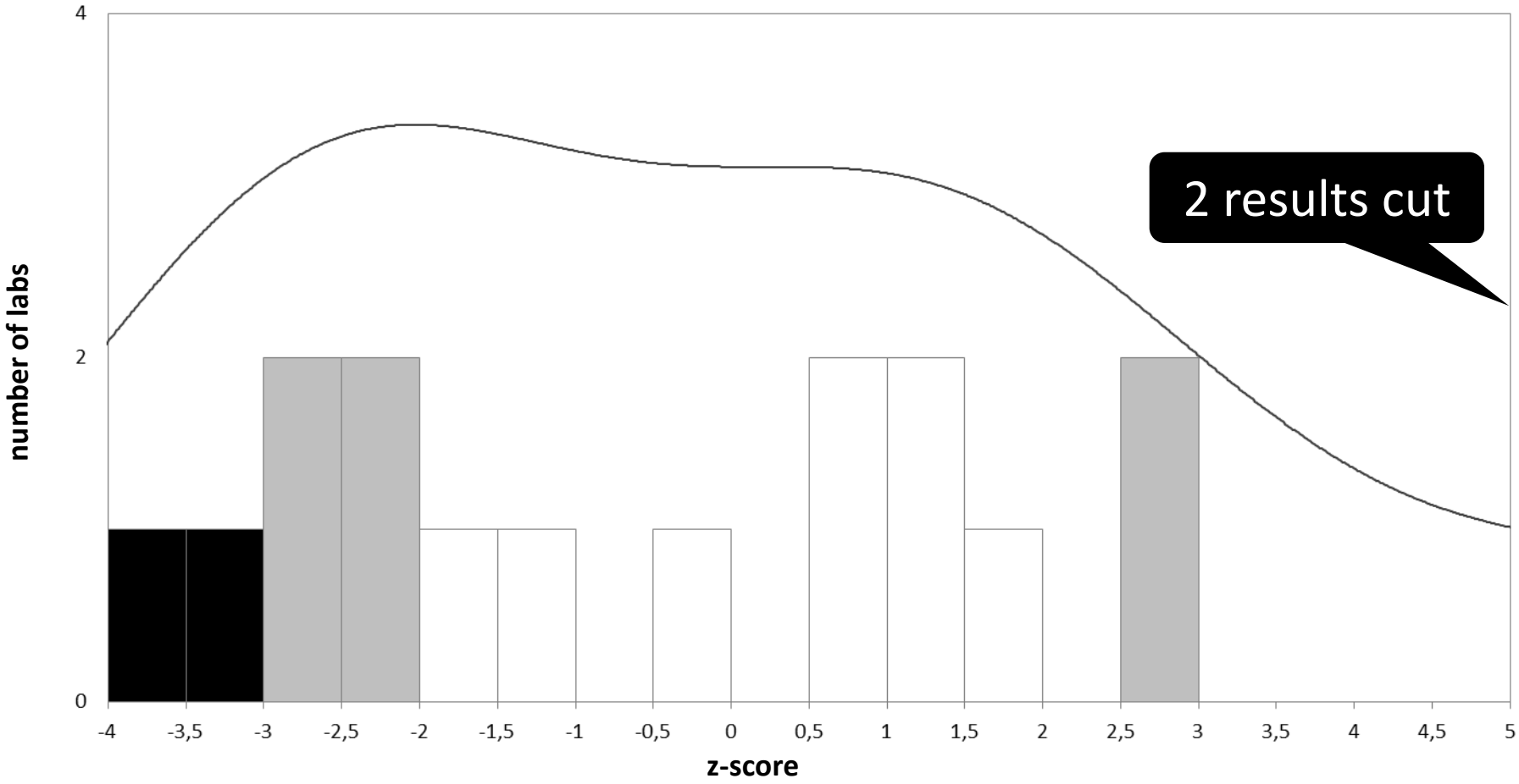


EURL-SRM

PHOSPHANE (PH3 SAMPLE)

Phosphane II („PH_3 sample“)

Results	**18**
False Neg.	
AV	*0.040* **[mg/kg]**
CV*	**74.8 %**
MRRL	**0.005 [mg/kg]**



UNCERTAINTY OF ASSIGNED VALUE

Compulsory Compounds

Compound	No. of Numerical Results	CV* [%]	Assigned Value (AV) [mg/kg]	Uncertainty of AV (UAV) [mg/kg]	UAV-Tolerance [mg/kg]	Judgement
Bromide ion	61	24.0%	15.3	0.58988	1.1517	passed
Cyromazine	78	23.5%	0.097	0.00323	0.0073	passed
Fluazifop	85	20.3%	0.049	0.00136	0.0037	passed
Glyphosate	83	22.6%	0.903	0.02798	0.0677	passed
Haloxyfop	81	20.4%	0.017	0.00048	0.013	passed
Mepiquat	84	22.9%	0.124	0.00387	0.0093	passed

EURL-SRM

UNCERTAINTY OF ASSIGNED VALUE

Optional Compounds

Compound	No. of Numerical Results	CV* [%]	Assigned Value (AV) [mg/kg]	Uncertainty of AV (UAV) [mg/kg]	UAV-Tolerance [mg/kg]	Judgement
2,4-DB	50	20.7%	0.183	0.00669	0.0137	passed
Diquat	29	52.8%	1.70	0.20868	0.1267	failed
Glufosinate	41	28.7%	0.192	0.01073	0.0144	passed
MPP	24	18.9%	0.188	0.00908	0.0141	passed
N-Acetyl-Glyphosate	18	21.1%	0.835	0.05185	0.0626	passed
Perchlorate	53	16.9%	0.100	0.00289	0.0075	passed
Phosphonic acid	42	24.3%	1.864	0.08723	0.1398	passed
Quizalofop	60	23.6%	0.052	0.00198	0.0039	passed
Phsophine I	11	93.1%	0.092	0.02517	0.0069	failed
Phosphine II	11	74.8%	0.040	0.00877	0.003	failed

EURL-SRM

OVERALL PERFORMANCE I: COMPULSORY COMPOUNDS

Compulsory compounds:

EU+EFTA

Compound	No. of Labs	FNs	AAZ	CV* [%]	☺ A	😐 Q	☹ U
Bromide ion	61	1	0.9	24.0%	90%	3%	6%
Cyromazine	78	1	1.0	23.5%	82%	10%	8%
Fluazifop	85	1	0.7	20.3%	97%	2%	1%
Glyphosate	83		0.8	22.6%	94%	2%	4%
Haloxyfop	81		0.7	20.4%	96%	2%	1%
Mepiquat	84	2	1.0	22.9%	88%	2%	9%

Optional Compounds:

EU+EFTA

Compound	No. of Labs	FNs	AAZ	CV* [%]	☺ A	😐 Q	☹ U
2,4-DB	50	2	0.8	20.7%	92%	2%	6%
Diquat	*29*	*1*	*1.7*	*52.8%*	*63%*	*17%*	*20%*
Glufosinate	41	3	1.2	28.7%	84%	5%	11%
MPP	24	1	1.1	18.9%	80%	8%	12%
N-Acetyl-Glyphosate	18	5	1.5	21.1%	74%	0%	26%
Perchlorate	53	2	0.9	16.9%	85%	5%	9%
Phosphonic acid	42	3	1.2	24.3%	80%	4%	16%
Quizalofop	60	2	0.9	23.6%	87%	8%	5%
Phsophine I	*11*		*2.4*	*93.1%*	*55%*	*0%*	*45%*
Phosphine II	*11*		*2.3*	*74.8%*	*45%*	*36%*	*18%*

EURL-SRM

OVERALL PERFORMANCE III

Rules for Category A:

EU+EFTA

- Analysed for at least 8 out of 9 compulsory pesticides
- Correctly found for at least 5 out of 6 compulsory pesticides present in test item
- No FPs

	No. of Labs	[%]
Category A	64	59 %
Category B	45	41 %

METHODS EMPLOYED BY EUPT PARTICIPANTS

EUPT-SRM 13 Methods employed	QuEChERS* (diff. versions)	QuPPe	SweEt	Dutch/ Mini-Luke/ S19	ChemElut	with Derivati-sation
2,4-D	91%	1%	3%	2%	2%	0%
Bentazone	91%	1%	4%	1%	3%	0%
Haloxyfop	90%	0%	4%	2%	2%	0%
Carbofuran	89%	1%	6%	3%	1%	0%
Fluazifop	89%	1%	5%	2%	2%	0%
Fenoxaprop	88%	0%	5%	2%	5%	0%
Quizalofop	87%	0%	6%	3%	3%	0%
2,4-DB	85%	2%	5%	4%	4%	0%
Cyromazine	44%	54%	3%	0%	0%	0%
Chlormequat	12%	88%	0%	0%	0%	0%
Mepiquat	11%	89%	0%	0%	0%	0%

Correcting for low recovery

EU+EFTA

METHODS EMPLOYED BY EUPT PARTICIPANTS

EUPT-SRM 13 Methods employed	QuEChERS* (diff. versions)	QuPPe	SweEt	Dutch/ Mini-Luke/ S19	Chem-Elut	with Derivatisation
Chlorate	0%	100%	0%	0%	0%	0%
N-Ac-Glufosinate	0%	100%	0%	0%	0%	0%
Perchlorate	0%	100%	0%	0%	0%	0%
Phosphonic Acid	0%	100%	0%	0%	0%	0%
Ethephon	1%	99%	0%	0%	0%	0%
Diquat	4%	96%	0%	0%	0%	0%
MPPA	0%	96%	0%	0%	0%	0%
Paraquat	4%	96%	0%	0%	0%	0%
N-Ac-Glyphosate	0%	95%	0%	0%	0%	0%
AMPA	0%	71%	0%	0%	0%	29%
Glufosinate	0%	69%	0%	0%	0%	29%
Glyphosate	0%	68%	0%	0%	0%	31%
Bromide	0%	33%	0%	0%	0%	52%

Mainly FMOC, some OPA

SRM12: 23% for bromide

Mainly Propylene oxide, some Ethylene oxide

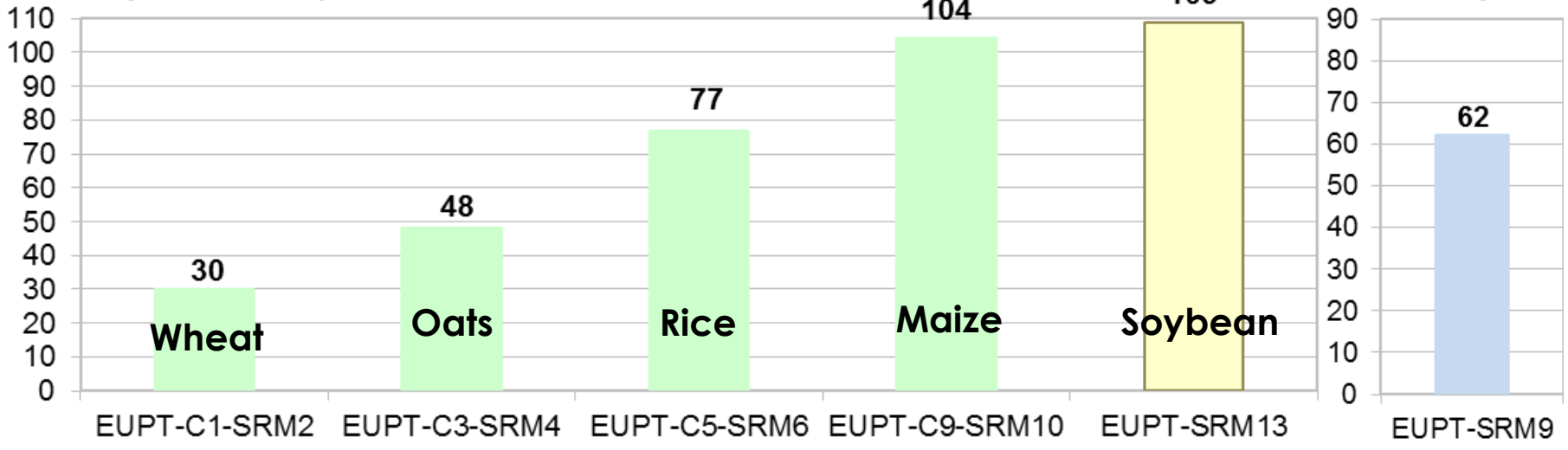
EUPT-SRM 1 (6) – 13

Overall Evaluation

EURL-SRM

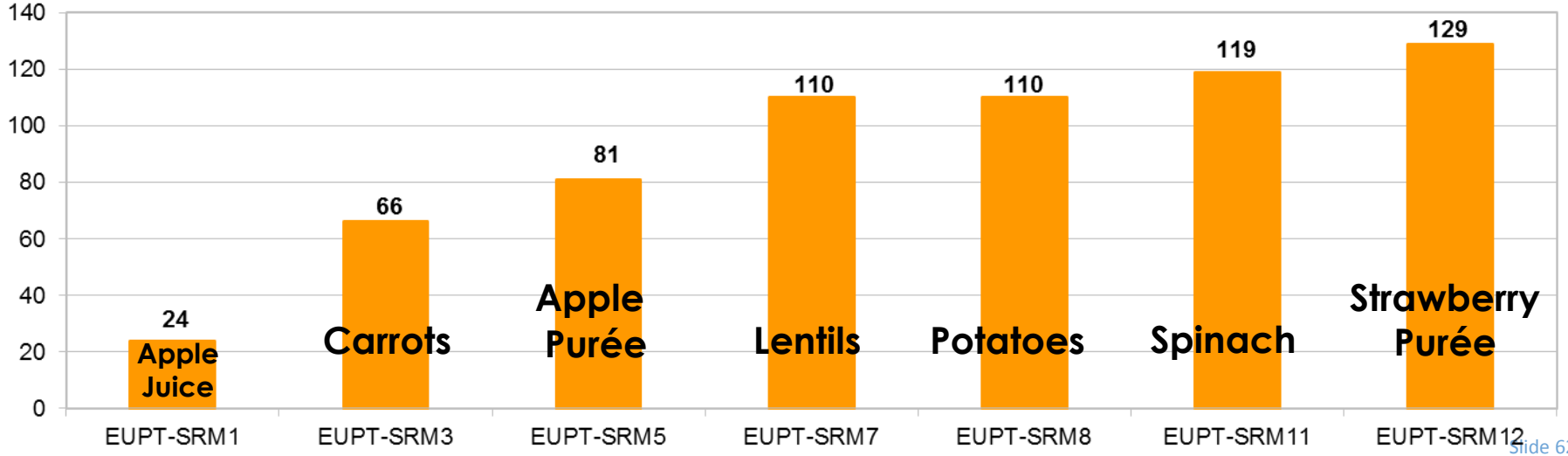
NO. OF LABS SUBMITTING RESULTS IN EUPT-SRMs

Cererals & Feed

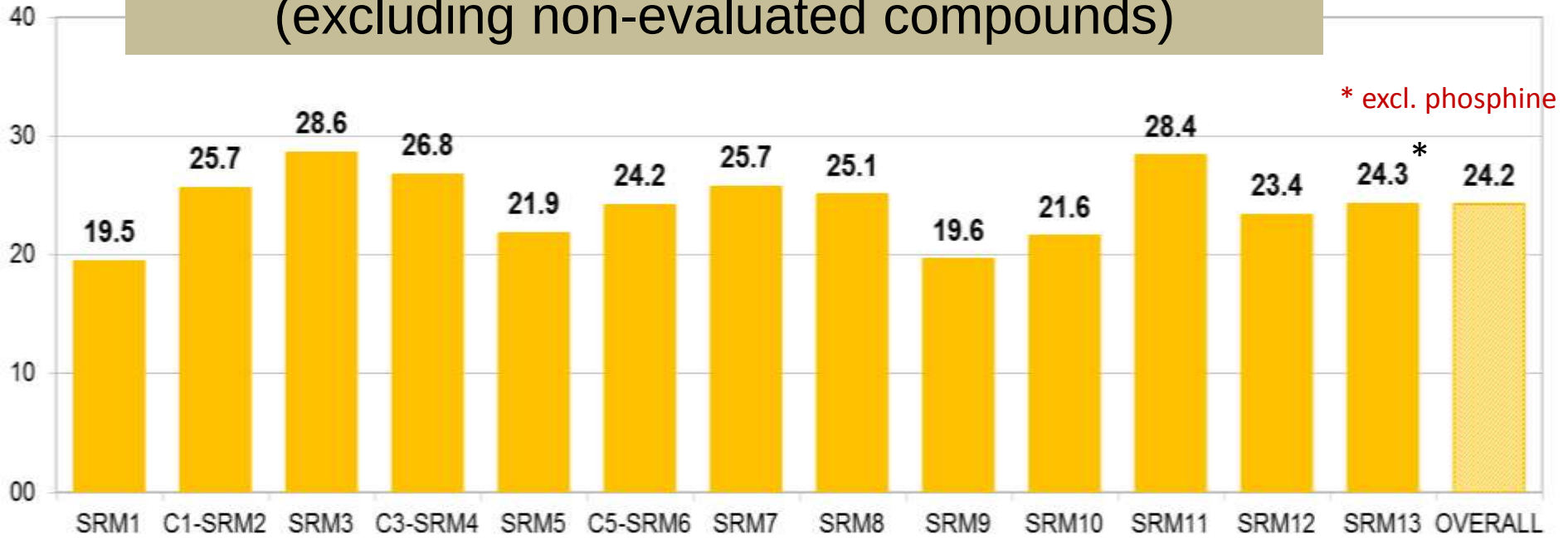


AO

Fruits, Vegetables and Pulses



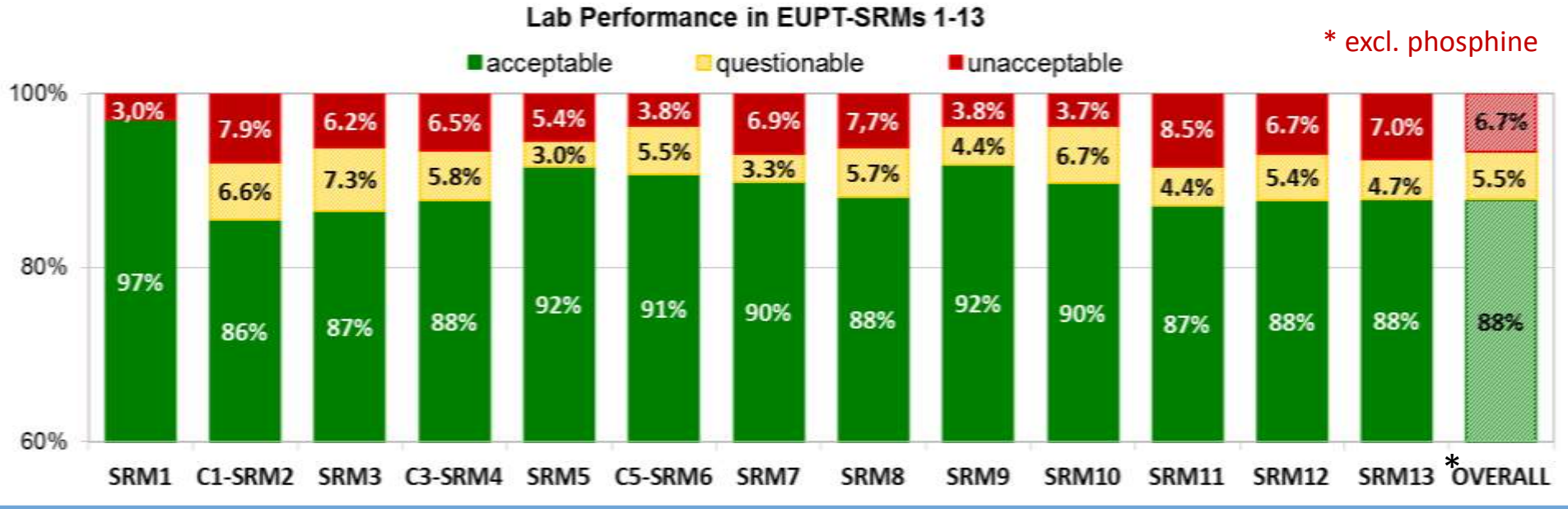
Robust standard deviation on average
(excluding non-evaluated compounds)



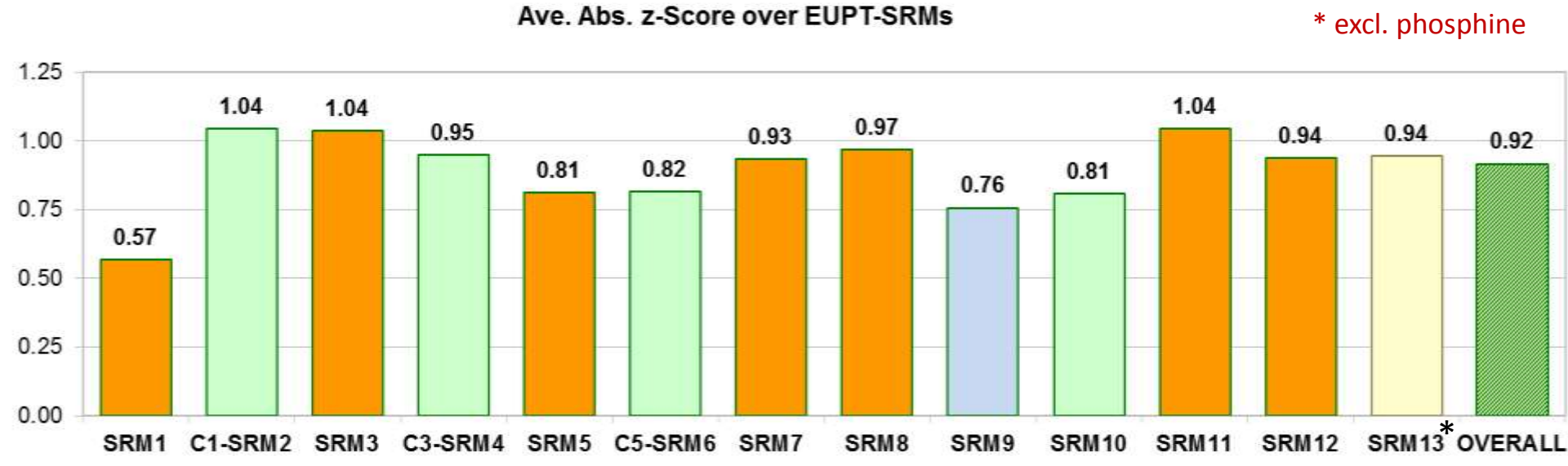
* excl. phosphine

EURL-SRM

OVERALL PERFORMANCE IN EUPT-SRMs 1-13



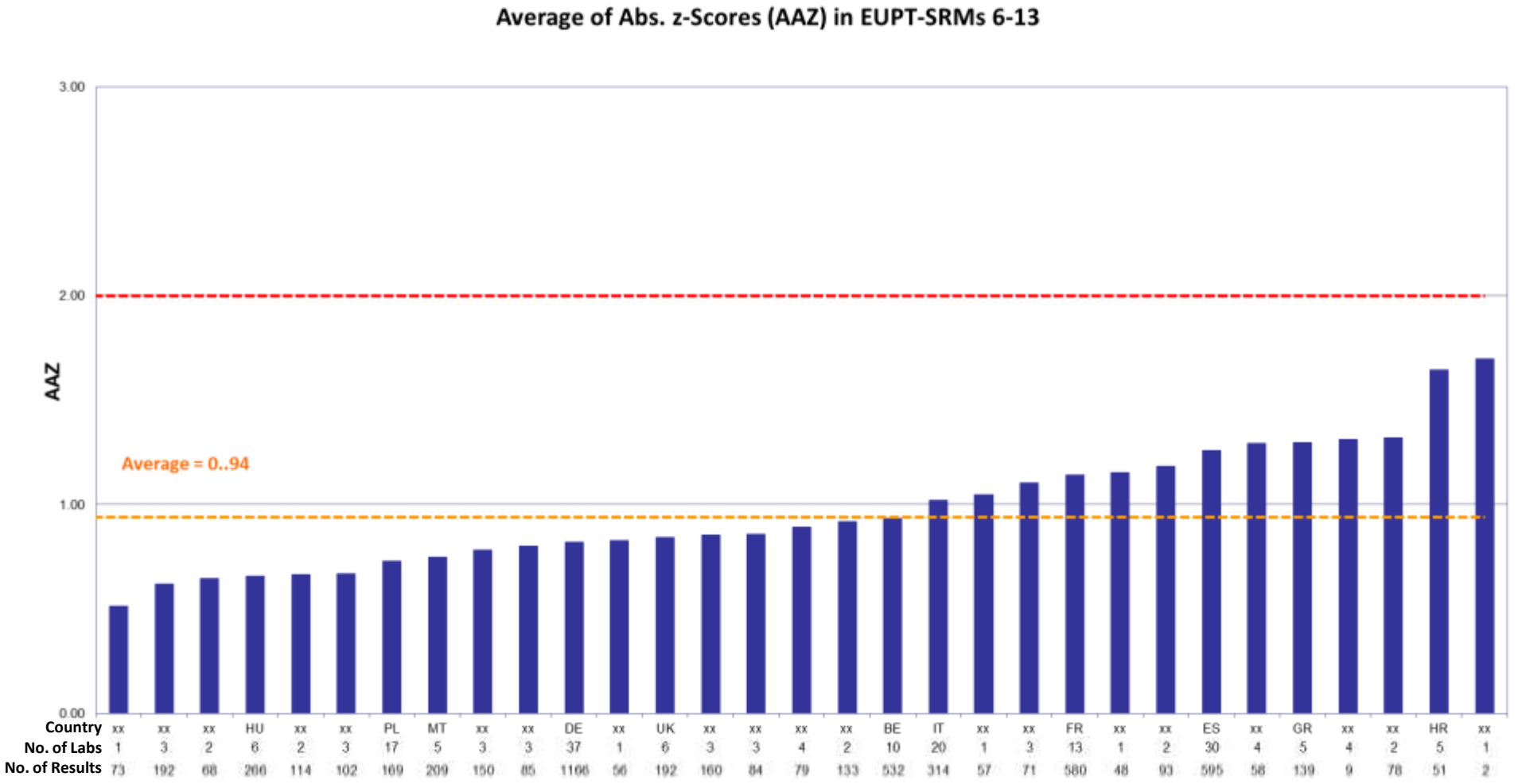
* excl. phosphine



* excl. phosphine

EURL-SRM

AAZ in EUPT-SRMs 6-13 (EU+EFTA)



Analytes evaluated for information only were excluded from the AAZ-calculation
Countries with less than 4 labs participating in the EUPT-SRM 1-13 are hidden.

EURL-SRM

PERFORMANCE BY COUNTRY (EUPT-SRM 6-13)

Analytes evaluated for information only were excluded.
Countries with less than 4 labs participating in the EUPT-SRM 6-13 are hidden.

Thank You
for Your Attention

www.eurl-pesticides.eu