EUPT-SRM11 Pesticide Residues in Spinach Homogenate

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EURL-SRM

SELECTION OF COMMODITY & PESTICIDES TO BE SPIKED

COMMODITY Selection (Spinach):

Decision of the **EUPT-Scientific Committee** meeting

Considerations for PESTICIDE SELECTION:

a) Pesticides in **Monitoring** programmes:

- MACP-Reg.: 2,4-D, Cyromazine, Dithiocarbamates, Dithianon, Pymetrozine …
- MACP-WD: BAC, DDAC, Chlorate, Fosetyl, Quizalofop, Triclopyr, MCPA ….

b) **Capabilities and expressed Interest of Labs**

- Communication with NRLs and OfLs

c) Opinion of the **EUPT-Scientific Committee**

- Selection of Pesticides for the Target Pesticide List

d) Opinion of the **EUPT-QC-Group**

- Selection of pesticides to be spiked and approx. levels

(also considering how analytes match together analytically)

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

TARGET PESTICIDE LIST

for the EUPT – SRM11 2016, Spinach Homogenate

update on 30.03.2016

Compounds Potentially Present in Test Item	In MACP	MRRL (mg/kg)
Compulsory Compounds (will be considered in Category A/B classification)		
2,4-D (free acid*)	MACP-Reg.	0.01
Cyromazine	MACP-Reg.	0.01
Dithiocarbamates (expressed as CS_2)	MACP-Reg.	0.03
Dodine	MACP-Reg.	0.01
Ethephon	MACP-Reg.	0.02
Fluazifop (free acid*)	MACP-Reg.	0.01
Glyphosate	MACP-Reg.	0.03
Haloxyfop (free acid*)	MACP-Reg.	0.01
TFNA (metabolite of flonicamid)	MACP-Reg.	0.01
TFNG (metabolite of flonicamid)	MACP-Reg.	0.01
Tolylfluanid (parent only)	MACP-Reg.	0.01
Optional Compounds (will NOT be considered in Category A/B classification)		
BAC-C10 (expressed as chloride salt)	MACP-WD	0.02
BAC-C12 (expressed as chloride salt)	MACP-WD	0.02
BAC-C14 (expressed as chloride salt)	MACP-WD	0.02
BAC-C16 (expressed as chloride salt)	MACP-WD	0.02
BAC-C18 (expressed as chloride salt)	MACP-WD	0.02
Chlorate (anion)	MACP-WD	0.02
DDAC-C10 (expressed as chloride salt)	MACP-WD	0.01
Dithianon SHIFT FROM COMPULSORY TO OPTIONAL	MACP-Reg.	0.01
Fosetyl	MACP-WD	0.02
Phosphonic acid	MACP-WD	0.05
MCPA (free acid*)	MACP-WD	0.01
MCPB (free acid*)	MACP-WD	0.01
Perchlorate (anion) NEW!	–	0.02
Pymetrozine NEW!	MACP-Reg.	0.01
Quizalofop (free acid*)	MACP-WD	0.01
Triclopyr	MACP-WD	0.01

MACP = EU Multi-Annual Coordinated Control Program;
MACP-Reg.: MACP Regulation; MACP-WD: MACP Working Document
* no hydrolysis

EUPT-SRM11 ORGANISATION

Registration for EUPT-SRM11:

8 Feb. - 11 March 2016

Sample Shipment:

4/5 May, 2016

Results Submission:

7 May – 20 May, 2016

Preliminary Report:

2 June, 2016

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

CALENDAR for the EUPT – SRM11

Spinach Homogenate

(update on 13 April, 2016)

Activity	Who ?	Dates
Opening of the EUPT-SRM11 Website with links to all relevant documents (List of obliged labs, Calendar, Target Pesticides List, General Protocol)	EURL-SRM	Jan. 2016
Registration via "EUPT-Registration Website" (Note: obliged OfLs MUST enter this Website and either register or give explanations for non-participation)	- Obliged OfLs from EU-MSs - OfLs from EFTA Countries - OfLs from EU-candidate C. - Labs from 3rd Countries	8 Feb. - 11 March 2016
Dispatch of EUPT-SRM11-Specific Protocol	EURL-SRM	March 2016
Preparation of EUPT-SRM11-Test Item (preliminary tests Spiking / Homogenization)	EURL-SRM	Jan. – March 2016
Homogeneity Tests	EURL-SRM	March – Apr. 2016
Stability Tests	EURL-SRM	March – May 2016
Shipment of EUPT-SRM11 Test Item (+reminder of upcoming parcel arrival)	EURL-SRM	4 Apr. 2016 (ES, PT) 5 Apr. 2016 (all other countries)
Confirmation of sample Receipt and acceptance via "EUPT-SRM11 Result Submission Website", (Sub-Page 0)	Participating Labs	within 48 h of receipt
Result Submission (Pesticide scope, Results, Method Info) in "EUPT-SRM11 Result Submission Website", (Sub-Pages 1 – 3)	Participating Labs	7 Apr. – 20 May 2016
Preliminary Report (only compilation of results)	EURL-SRM	June 2016
EUPT Evaluation Meeting	EUPT-SC, DG-SANTE	-
Survey to collect reasons for underperformance and missing information on methods	EURL-SRM / Participating Labs	June 2016
Final Report	EURL-SRM	Dec. 2016

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 still please check periodically our website for possible updates in case the email does not get through to you.
Contact: eurl-srm@cvuas.bwl.de

The EUPT-SRM Team

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EURL-SRM VOTING FOR PESTICIDE TARGET LIST

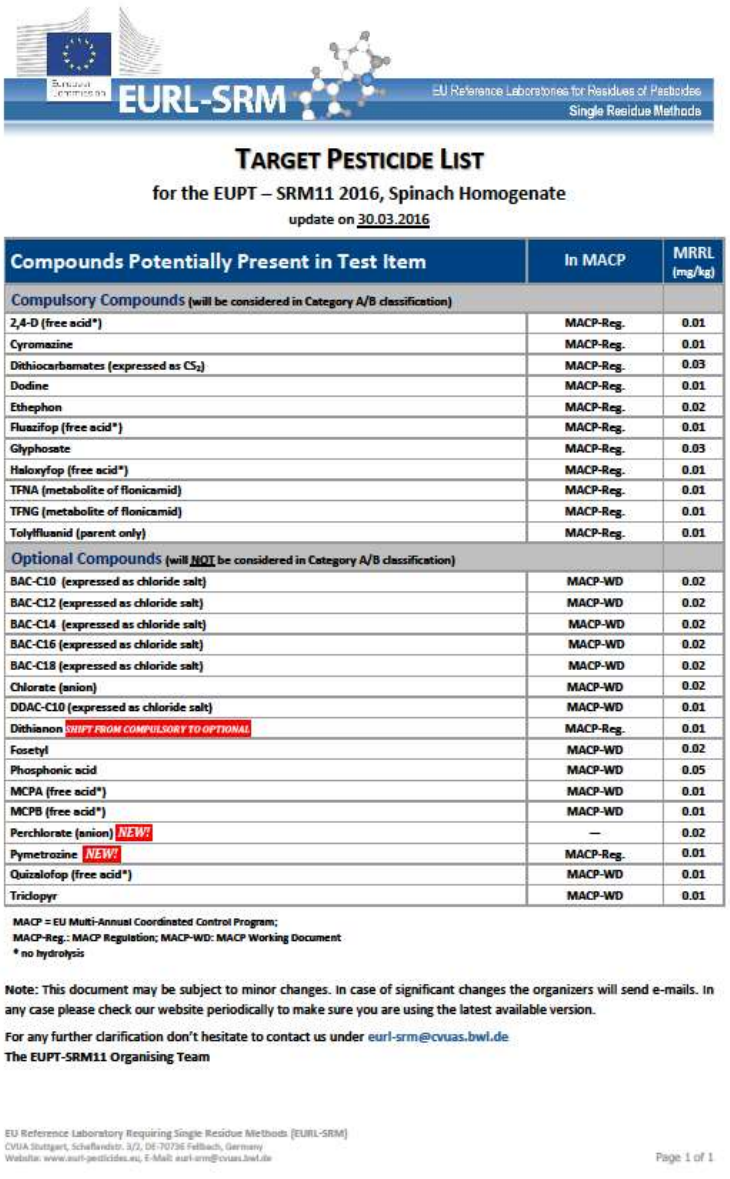
Compound	Analytical group	MRM/ SRM Comp.	RD	MRM/ SRM Full RD	Compound present in previous EUPT-SRMs	RELE-VANCE Findings VEGIES	RELE-VANCE Findings SPINACH	RELE-VANCE USAGE SPINACH +LEAFY VEGIES	Approved EU (in general)	Monitoring (Regulation / Working Document)	Notes 1	VOTE Total Pts = YES-NO (click above to see	INCLUDE/ EXCLUDE from TPL FINAL DECISION by ORGANIZE	METHOD Extraction	METHOD Measurement	Comment on final decission by ORGANIZER
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)	SRM	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)	interm.	interm.		Approved	Reg.	only parent	11	Include Mandatory	QuEChERS or QuEChERS-Acidic	ESI-Neg	
4-CPA	Acid	MRM/SRM	NONE	SRM		Minor	no					-8	Exclude	QuEChERS or QuEChERS-Acidic	ESI-Neg	
Abamectin	QuEChERS with attn.	MRM/SRM	Abamectin (sum of avermectin B1a, avermectinB1b and delta-8,9 isomer of avermectin B1a) (F)	MRM/SRM	SRM03 (mandatory; Qn: 23.4) | SRM05 (mandatory; Qn: 24.3)	interm.	no	yes	Approved	Reg.		3	Include Mandatory?	QuEChERS or QuEChERS-Acidic	ESI-Pos.	
Bentazone	Acid	MRM/SRM	Bentazone (Sum of bentazone, its salts and 6-hydroxy (free and conjugated) and 8-hydroxy bentazone (free and conjugated), expressed as bentazone) (R)	SRM	SRM10 (optional; Qn: 18.5)	Minor	no	yes	Approved		only parent	10	Exclude	QuEChERS or QuEChERS-Acidic	ESI-Neg	exclude as not in MACP reg or WD
BAC (C10,C12,C14, C16, C18)	QuEChERS with attn.		Benzalkonium chloride (mixture of alkylbenzyldimethylammonium chlorides with alkyl chain lengths of C8, C10, C12, C14, C16 and C18)		BAC-C12: SRM08 (optional; Qn: 24.1) | SRM09 (mandatory; Qn: 17.6) BAC-C14: SRM09 (mandatory; Qn: 17.9)	high	high		Not Approved	WD	Few labs	11	Include OPTIONAL	QuEChERS or QuEChERS-Acidic	ESI-Pos.	
Bromide (inorg.)	Individual	SRM	Bromide ion	SRM	SRM06 (mandatory; Qn: 8.6) | SRM07 (mandatory; Qn: 18.0)	(high)	(high)	yes	Not Approved	Reg.		0	Exclude?	Individual OR QuPPe	GC after deriv. OR ESI-Neg	Although in MACP-Reg. not included, no majority in voting
Bromoxynil	Acid	MRM/SRM	Bromoxynil and its salts, expressed as bromoxynil	MRM/SRM	SRM10 (optional; Qn: 17.0)	Minor	Minor	yes	Approved			9	Exclude	QuEChERS or QuEChERS-Acidic	ESI-Neg	exclude as not in MACP reg or WD
Captan	QuEChERS with attn. BaseSensit.	MRM/SRM	Captan (R)	MRM/SRM	SRM08 (mandatory; Qn: 26.0)	Minor	no	yes	Approved	Reg.	degrades at high pH	11	Include Mandatory	QuEChERS-Acidic	GC	
Carbosulfan	QuEChERS	MRM/SRM	Carbofuran (sum of carbofuran (including any carbofuran generated from carbosulfan, benfuracarb or furathiocarb)	MRM/SRM		Minor	no		Not	Reg.	- Degrades to Carbofura - Part of RD of Cf - Low MRLs	-4	Exclude?	QuEChERS-	ESI-Pos.	Although in MACP-Reg. not included due to strongly negative voting
Furathiocar			as carbofuran) (R)								Vegetables					Although in MACP-Reg. not included due to strongly negative voting
Benfuracarb	QuEChERS with hydrol.	MRM/SRM	Carbofuran (sum of carbofuran (including any carbofuran generated from carbosulfan, benfuracarb or furathiocarb) and 3-OH carbofuran expressed as carbofuran) (R)	MRM/SRM			no		Not Approved	Reg.	- Degrades to Carbofura - Part of RD of Cf - Low MRLs - Toxicologically critical - Cf occationally found in Vegetables	-4	Exclude?	QuEChERS-Modified	ESI-Pos.	Although in MACP-Reg. not included due to strongly negative voting
Chlorate	PolarNeg	SRM	NONE	SRM	SRM09 (optional; Qn: 17.0)	high	high			WD	Provisional MRLs and RD Few labs analyzing	7	Include OPTIONAL	QuPPe	ESI-Neg	
Chlormequat	PolarPos	SRM	Chlormequat	SRM	SRM01 (mandatory; Qn: 16.0) | SRM02 (mandatory; Qn: 32.0) | SRM04 (mandatory; Qn: 25.8) | SRM09 (mandatory; Qn: 19.8) |	high	no		Approved	Reg.		8	Include Mandatory	QuPPe	ESI-Pos.	

Voting considering different aspects on use, residue findings MACP, lab capabilities, method fits …

EURL-SRM TARGET PESTICIDES LIST

	In Target List
Compulsory	11
Optional*	16

** Optional = not considered in lab-categorization based on scope



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

TARGET PESTICIDE LIST

for the EUPT – SRM11 2016, Spinach Homogenate

update on 30.03.2016

Compounds Potentially Present in Test Item	In MACP	MRRL (mg/kg)	
Compulsory Compounds (will be considered in Category A/B classification)			
2,4-D (free acid*)	MACP-Reg.	0.01	Compulsory
Cyromazine	MACP-Reg.	0.01	
Dithiocarbamates (expressed as CS_2)	MACP-Reg.	0.03	
Dodine	MACP-Reg.	0.01	
Ethephon	MACP-Reg.	0.02	
Fluazifop (free acid*)	MACP-Reg.	0.01	
Glyphosate	MACP-Reg.	0.03	
Haloxyfop (free acid*)	MACP-Reg.	0.01	
TFNA (metabolite of flonicamid)	MACP-Reg.	0.01	
TFNG (metabolite of flonicamid)	MACP-Reg.	0.01	
Tolylfluanid (parent only)	MACP-Reg.	0.01	
Optional Compounds (will NOT be considered in Category A/B classification)			
BAC-C10 (expressed as chloride salt)	MACP-WD	0.02	Optional
BAC-C12 (expressed as chloride salt)	MACP-WD	0.02	
BAC-C14 (expressed as chloride salt)	MACP-WD	0.02	
BAC-C16 (expressed as chloride salt)	MACP-WD	0.02	
BAC-C18 (expressed as chloride salt)	MACP-WD	0.02	
Chlorate (anion)	MACP-WD	0.02	
DDAC-C10 (expressed as chloride salt)	MACP-WD	0.01	
Dithianon SHIFT FROM COMPULSORY TO OPTIONAL	MACP-Reg.	0.01	
Fosetyl	MACP-WD	0.02	
Phosphonic acid	MACP-WD	0.05	
MCPA (free acid*)	MACP-WD	0.01	
MCPB (free acid*)	MACP-WD	0.01	
Perchlorate (anion) NEW!	–	0.02	
Pymetrozine NEW!	MACP-Reg.	0.01	
Quizalofop (free acid*)	MACP-WD	0.01	
Triclopyr	MACP-WD	0.01	

MACP = EU Multi-Annual Coordinated Control Program;
MACP-Reg.: MACP Regulation; MACP-WD: MACP Working Document
* no hydrolysis

Note: This document may be subject to minor changes. In case of significant changes the organizers will send e-mails. In any case please check our website periodically to make sure you are using the latest available version.

For any further clarification don't hesitate to contact us under eurl-srm@cvuas.bwl.de
The EUPT-SRM11 Organising Team

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TARGET PESTICIDES LIST

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BAC-C14 (expressed as chloride salt)	MACP-WD	0.02
BAC-C16 (expressed as chloride salt)	MACP-WD	0.02
BAC-C18 (expressed as chloride salt)	MACP-WD	0.02
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TARGET PESTICIDES LIST

	in TARGET LIST	in TEST ITEM				
		Incurred (formulation sprayed in greenhouse)		**Spiked** (postharvest w. anal. std)		Sum
Compulsory	*11*	Cyromazine DTCs (Propineb) Dodine TFNA (Flonicamid) TFNG (Flonicamid)	5	Tolylfluanid	1	6
Optional	*16*	Pymetrozine* Dithianon Phosphonic acid Chlorate** Perchlorate**	5	BAC-C14 Triclopyr Quizalofop	3	8
TOTAL	*27*	**10**		**4**		14

* Pymetrozine was spiked following insect threat
** Chlorate and Perchlorate contained in Irrigation water

} Contained both in blank and Test Item

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PREPARATION OF TEST ITEM

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PREPARATION OF TEST ITEM

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HOMOGENEITY TEST

COMPULSORY Compounds

	Cyromazine	DTCs as CS_2	Dodine	TFNA	TFNG	Tolylfluanid
sample	Concentration [mg/kg]					
010	1.447 / 1.656	1.304 / 1.045	1.286 / 1.298	0.841 / 0.821	0.519 / 0.468	0.881 / 0.792
024	1.385 / 1.564	1.347 / 1.213	1.295 / 1.265	0.841 / 0.795	0.496 / 0.519	1.333 / 0.815
053	1.551 / 1.611	1.229 / 1.423	1.338 / 1.329	0.838 / 0.896	0.467 / 0.488	0.935 / 1.053
062	1.527 / 1.424	1.508 / 1.586	1.273 / 1.272	0.853 / 0.846	0.487 / 0.490	0.939 / 0.835
081	1.517 / 1.593	1.432 / 1.479	1.309 / 1.327	0.761 / 0.865	0.492 / 0.475	1.104 / 1.084
109	1.564 / 1.651	1.431 / 1.431	1.368 / 1.321	0.806 / 0.838	0.457 / 0.490	1.086 / 0.936
115	1.465 / 1.534	1.492 / 1.464	1.247 / 1.239	0.815 / 0.828	0.505 / 0.481	0.842 / 0.941
128	1.562 / 1.671	1.675 / 1.497	1.301 / 1.292	0.830 / 0.808	0.482 / 0.480	0.803 / 0.744
166	1.59 / 1.722	1.561 / 1.608	1.275 / 1.196	0.776 / 0.833	0.468 / 0.489	1.111 / 0.827
185	1.679 / 1.503	1.411 / 1.336	1.271 / 1.382	0.915 / 0.812	0.473 / 0.504	0.976 / 0.793
mean	1.561	1.424	1.294	0.831	0.486	0.942
S_{sam}^2	0.00×10^{0}	1.42×10^{-2}	8.24×10^{-4}	0.00×10^{0}	0.00×10^{0}	0.00×10^{0}
c	3.43×10^{-2}	3.00×10^{-2}	1.88×10^{-2}	8.93×10^{-3}	2.85×10^{-3}	3.22×10^{-2}
	passed	passed	passed	passed	passed	passed

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HOMOGENEITY TEST

OPTIONAL Compounds

	BAC-C14	Chlorate	Dithianon	Phosphonic acid	Perchlorate	Pymetrozine	Quizalofop	Triclopyr
sample	Concentration [mg/kg]							
010	0.307 / 0.289	2.232 / 2.374	4.449 / 4.340	9.386 / 9.140	0.264 / 0.255	0.529 / 0.543	0.162 / 0.147	0.188 / 0.18
024	0.437 / 0.332	2.422 / 2.265	3.186 / 3.666	9.464 / 9.818	0.275 / 0.269	0.473 / 0.504	0.22 / 0.167	0.24 / 0.211
053	0.28 / 0.371	2.338 / 2.254	3.274 / 3.951	9.258 / 9.217	0.26 / 0.248	0.507 / 0.536	0.157 / 0.172	0.194 / 0.194
062	0.336 / 0.284	2.181 / 2.283	4.305 / 4.381	9.315 / 9.158	0.26 / 0.254	0.522 / 0.442	0.162 / 0.154	0.191 / 0.19
081	0.42 / 0.415	2.34 / 2.294	3.310 / 3.236	10.026 / 9.932	0.27 / 0.265	0.56 / 0.477	0.231 / 0.201	0.238 / 0.244
109	0.361 / 0.335	2.394 / 2.312	4.894 / 3.810	9.756 / 10.448	0.259 / 0.251	0.521 / 0.489	0.174 / 0.174	0.192 / 0.211
115	0.327 / 0.335	2.329 / 2.353	3.766 / 2.959	8.909 / 9.14	0.268 / 0.263	0.495 / 0.469	0.162 / 0.166	0.198 / 0.199
128	0.278 / 0.272	2.264 / 2.259	3.272 / 4.173	9.073 / 8.726	0.261 / 0.262	0.501 / 0.518	0.145 / 0.14	0.194 / 0.174
166	0.342 / 0.281	2.408 / 2.322	3.787 / 3.755	9.360 / 9.702	0.251 / 0.264	0.474 / 0.518	0.185 / 0.165	0.213 / 0.192
185	0.336 / 0.281	2.439 / 2.266	3.550 / 3.650	9.485 / 10.494	0.279 / 0.275	0.531 / 0.511	0.184 / 0.154	0.211 / 0.186
mean	0.331	2.316	3.786	9.490	0.263	0.506	0.171	0.202
S_{sam}^2	1.05×10^{-3}	0.00×10^{0}	9.84×10^{-2}	1.31×10^{-1}	4.36×10^{-5}	0.00×10^{0}	2.94×10^{-4}	2.62×10^{-4}
c	2.67×10^{-3}	6.23×10^{-2}	3.21×10^{-1}	1.05×10^{0}	7.60×10^{-4}	3.69×10^{-3}	5.92×10^{-4}	5.68×10^{-4}
$S_{sam}^2 < c$	passed	passed	passed	passed	passed	passed	passed	passed

EURL-SRM

STABILITY TEST

COMPULSORY Compounds

Sample	Cyromazine [mg/kg]			DTCs as CS_2 [mg/kg]			Dodine [mg/kg]		
	25.04.2016	12.05.2016	22.06.2016	08.04.2016	13.05.2016	25.05.2016	06.04.2016	12.05.2016	25.05.2016
24 (DTCs: 53)	1.669	1.773	1.689	1.326	1.371	1.224	1.145	1.155	1.135
81(DTCs: 109)	1.655	1.678	1.692	1.431	1.234	1.394	1.255	1.195	1.210
166 (DTCs: 185)	1.762	1.712	1.812	1.374	1.362	1.265	1.170	1.180	1.180
Mean	**1.695**	**1.721**	**1.731**	**1.377**	**1.322**	**1.294**	**1.190**	**1.177**	**1.175**
% Difference (vs. 1st analysis)	—	**-1.49 %**	**-2.08 %**	—	**-3.96 %**	**-6.00 %**	—	**-1.12 %**	**-1.26 %**
Diff (mean)		**0.025**	**0.035**		**0.055**	**0.083**		**0.013**	**0.015**
0,3* FFP-SD		**0.127**	**0.127**		**0.103**	**0.103**		**0.089**	**0.089**
Judgement		**passed**	**passed**		**passed**	**passed**		**passed**	**passed**

Sample	TFNA [mg/kg]			TFNG [mg/kg]			Tolylfluanid [mg/kg]		
	06.04.2016	12.05.2016	25.05.2016	06.04.2016	12.05.2016	25.05.2016	06.04.2016	12.05.2016	25.05.2016
24	0.818	0.815	0.800	0.507	0.495	0.475	1.100	1.070	1.110
81	0.813	0.800	0.775	0.484	0.470	0.445	1.120	1.070	1.020
166	0.805	0.815	0.780	0.479	0.495	0.455	1.020	0.990	1.145
Mean	**0.812**	**0.810**	**0.785**	**0.490**	**0.487**	**0.458**	**1.080**	**1.043**	**1.092**
% Difference (vs. 1st analysis)	—	**-0.23 %**	**-3.31 %**	—	**-0.67 %**	**-6.45 %**	—	**-3.40 %**	**1.08 %**
Diff (mean)		**0.002**	**0.027**		**0.003**	**0.032**		**0.037**	**0.012**
0,3* FFP-SD		**0,061**	**0,061**		**0.037**	**0.037**		**0.081**	**0.081**
Judgement		**passed**	**passed**		**passed**	**passed**		**passed**	**passed**

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STABILITY TEST

OPTIONAL Compounds

Sample	BAC-C14 [mg/kg]			Chlorate [mg/kg]			Dithianon [mg/kg]			Perchlorate [mg/kg]		
	06.04.2016	12.05.2016	25..05.2016	05.04.2016	12.05.2016	25..05.2016	06.04.2016	12.05.2016	25.05.2016	05.04.2016	12.05.2016	25..05.2016
24	0.384	0.346	0.369	2.343	2.637	2.535	3.820	3.300	2.815	0.247	0.239	0.250
81	0.418	0.362	0.328	2.317	2.432	2.487	3.470	3.805	3.185	0.251	0.223	0.250
166	0.311	0.328	0.341	2.365	2.435	2.421	3.090	3.540	3.260	0.243	0.229	0.238
Mean	**0.371**	**0.346**	**0.346**	**2.342**	**2.501**	**2.481**	**3.460**	**3.548**	**3.087**	**0.247**	**0.230**	**0.246**
% Difference (vs. 1st Analysis)	—	**-6,82 %**	**-6,68 %**	—	**6.80 %**	**5.93 %**	—	**2.55 %**	**-10.79 %**	—	**-6.74 %**	**-0.38 %**
Diff (mean)		**0.025**	**0.025**		**0.159**	**0.139**		**0.088**	**0.373**		**0.017**	**0.001**
0,3* FFP-SD		**0.028**	**0.028**		**0,176**	**0,176**		**0.260**	**0.260**		**0.019**	**0.019**
Judgement		**passed**	**passed**		**passed**	**passed**		**passed**	**failed**		**passed**	**passed**

Sample	Phosphonic acid [mg/kg]			Pymetrozine [mg/kg]			Quizalofop [mg/kg]			Triclopyr [mg/kg]		
	05.04.2016	12.05.2016	25..05.2016	25.04.2016	12.05.2016	22.06.2016	06.04.2016	12.05.2016	25.05.2016	06.04.2016	12.05.2016	25.05.2016
24	10.151	9.838	10.624	0.454	0.469	0.433	0.194	0.174	0.205	0.226	0.210	0.215
81	10.116	9.579	10.504	0.475	0.489	0.473	0.216	0.192	0.184	0.241	0.215	0.210
166	10.125	9.567	9.737	0.506	0.459	0.470	0.175	0.181	0.177	0.202	0.215	0.200
Mean	**10.131**	**9.661**	**10.288**	**0.478**	**0.472**	**0.459**	**0.195**	**0.182**	**0.189**	**0.223**	**0.213**	**0.208**
% Difference (vs. 1st analysis)	—	**-4.63 %**	**1.56 %**	—	**-1.29 %**	**-4.11 %**	—	**-6.54 %**	**-3.14 %**	—	**-4.35 %**	**-6.59 %**
Diff (mean)		**0.469**	**0.158**		**0.006**	**0.020**		**0.013**	**0.006**		**0.010**	**0.015**
0,3* FFP-SD		**0.760**	**0.760**		**0.036**	**0.036**		**0.015**	**0.015**		**0.017**	**0.017**
Judgement		**passed**	**passed**		**passed**	**passed**		**passed**	**passed**		**passed**	**passed**

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

EURL-SRM

HOMOGENEITY + STABILITY TEST (OVERVIEW)

Compulsory Compounds:

Compound	Homog. Test	Stability Test
Cyromazine	passed	passed
DTM as CS2	passed	passed
Dodine	passed	passed
TFNA	passed	passed
TFNG	passed	passed
Tolylfluanid	passed	passed

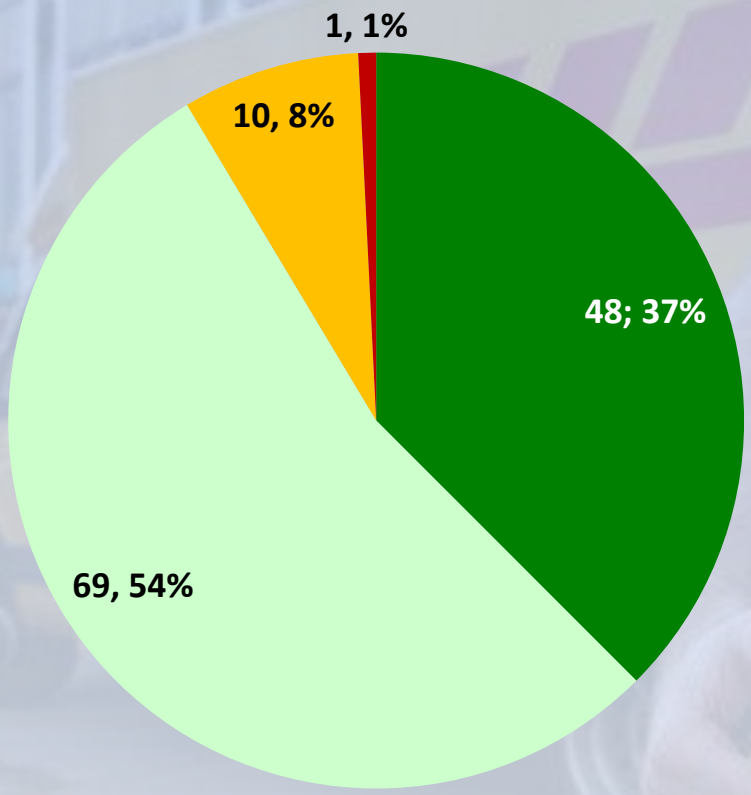
Optional Compounds:

Compound	Homog. Test	Stability Test
BAC-C14	passed	passed
Chlorate	passed	passed
Dithianon	passed	(failed)
Phosphonic acid	passed	passed
Perchlorate	passed	passed
Pymetrozine	passed	passed
Quizalofop	passed	passed
Triclopyr	passed	passed

EURL-SRM

STABILITY DURING SHIPPING

Shipping Duration



1 day: 18 (14 %) Labs in ES/PT
30 (23 %) Labs other EU/EFTA

2 days and 3 days:
mainly due to bird strike

1 day + 2 days = 91 %

6 days = due to customs declaration

If a 2nd shipment was required/necessary, duration was calculated for the 2nd shipment.

The 10 Labs having received their samples after 3 days did not show a particular trend (10, 15, 23, 51, 56, 62, 113, 114,115, 122)

EURL-SRM

TRANSPORT SIMULATION TEST -1

COMPULSORY Compounds

	Cyromazine	Dithiocarbamates	Dodine	TFNA	TFNG	Tolylfluanid
	Mean Concentration @ n=3 [mg/kg]					
Day 2	1.836	0.986	1.268	0.806	0.484	0.502
Day 3	1.739	0.953	1.260	0.790	0.472	0.459
Day 6	1.788	0.873	1.220	0.879	0.476	0.041
Deviation [%]						
Day 3 vs. Day 2	-5.3 %	-3.4 %	-0.6 %	-2.0 %	-2.4 %	-8.6 %
Day 6 vs. Day 2	-2.6 %	-11.4 %	-3.8 %	9.0 %	-1.6 %	-91.9 %

The content of 4 randomly chosen test items was combined in a larger container, mixed thoroughly (to achieve a good homogeneity) and refilled into bottles. During this process the material thawed extensively, which explains the extensive **losses of the vulnerable compounds tolylfluanid and dithianon** compared to the results of the original samples. Four parcels, each with one of the remixed and refilled test item and one bottle blank material, were **packed in the same way as the real packages to the participants** and sent by DHL Express to the EURL-SRM for the transport stability test. The four parcels arrived the EURL-SRM within 24 hours (day1) , and dry ice was still in the boxes. The parcel of day1 was put in the freezer but not analyzed (sent to an OfL as repetitive shipment). The other three parcels were left in the laboratory at ambient temperature for additional 1 (day2), 2 (day3) and 5 days (day6) and then put in the freezer at −18 °C till the day of analysis (8 July, 2016). **On day 2 the sample was still frozen. On day 3 it was partly frozen, on day 6 it was thawed and at room temperature.**

EURL-SRM

TRANSPORT SIMULATION TEST -2

OPTIONAL Compounds

	BAC-C14	Chlorate	Dithianon	Phosphonic acid	Perchlorate	Pymetrozine	Quizalofop	Triclopyr
	Mean Concentration @ n=3 [mg/kg]							
Day 2	0.277	2.465	2.792	11.303	0.223	0.501	0.176	0.191
Day 3	0.275	2.341	2.244	10.793	0.218	0.465	0.179	0.192
Day 6	0.289	2.017	0.034	9.762	0.209	0.426	0.170	0.249
Deviation [%]								
Day 3 vs. Day 2	-0.4 %	-5.0 %	-19.6 %	-4.5 %	-2.0 %	-7.2 %	1.5 %	0.7 %
Day 6 vs. Day 2	4.6 %	-8.2 %	-98.8 %	-13.6 %	-6.2 %	-15 %	-3.6 %	30.3 %

To be rechecked

EURL-SRM

PARTICIPATING LABS / COUNTRIES

		Labs submitting results	Registered WITHOUT submitting results
EU		118	5
EFTA		1	-
3rd Countries + EU Candidates		2	-
	SUM	121	5

EURL-SRM PARTICIPATING LABS / COUNTRIES

EU Country (Contracting)	Registered for PT		Submitted Results	
	Total	NRL-SRM	Total	NRL-SRM
AT	3	1	3	1
BE	7	1	6	1
BE / FR / LU	1		1	
BG	1	1	1	1
CY	1	1	1	1
CZ	3	1	3	1
DE	20	1	20	1
DK	2	1	2	1
EE	2	1	2	1
ES	16	2	16	2
FI	2	2	2	2
FR	8	1	8	1
GR	5	2	5	2
HR	3		3	
HU	4	1	4	1
IE	1	1	1	1
IT	13	1	11	1
LT	2	1	2	1
LU	1	1	1	1
LV	1	1	1	1
MT*	1		1	
NL	1	1	1	1
PL	8	1	8	1
PT	3	1	3	1
RO	2	1	2	1
SE	2	1	2	1
SI	3	1	3	1
SK	1	1	1	1
UK	3		3	
UK / MT	3	1	2	1
EU-Total	123	29	119	29

Countries	Registered for PT	Submitted results
Norway	1	1
EFTA-Total	1	1
Egypt	1	1
Serbia	1	1
3rd Countries + EU-Candidates	2	2

* MT subcontracts FERA (UK) as Proxy-NRL + Eurofins (DE) + LGC Teddington (UK) + Agrofood Laboratory (ES) for routine controls

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

Countries with no NRL-SRMs participating:

HR *"NRL-SRM not yet appointed"*

EURL-SRM

COVERAGE OF PT-COMPOUNDS BY LABS

Compulsory compounds

Compounds Present in Test Item

Compound	No. of Labs targeting	% (out of 120* labs)
DTCs	95	79%
Cyromazine	87	73%
Tolylfluanid	87	73%
Dodine	83	69%
TFNA	63	53%
TFNG	63	53%

NOT present

Compound	No. of Labs targeting	% (out of 120* labs)
2,4-D	93	78%
Haloxyfop	89	74%
Fluazifop	86	72%
Ethephon	71	59%
Glyphosate	71	59%

Coverage

- ≥ 80 %
- 50-79 %
- 25-49 %
- <25 %

*: 119 EU + 1 EFTA labs submitting results

EURL-SRM

FREQUENCY OF ANALYSIS

Optional Compounds

Present in Test Item

Compounds	No. of Labs targeting	% (out of 120* labs)
Pymetrozine*	62	52%
Triclopyr*	62	52%
BAC-C14	58	48%
Quizalofop*	58	48%
Chlorate	45	38%
Perchlorate	45	38%
Dithianon*	39	33%
Phosphonic acid	39	33%

NOT present in Test Item

Compounds	No. of Labs targeting	% (out 120* labs)
MCPA	85	71%
MCPB	61	51%
BAC-C12	59	49%
BAC-C16	57	48%
BAC-C10	56	47%
DDAC-C10	56	47%
Fosetyl	46	38%
BAC-C18	32	27%

*: Analytes for the first time in an EUPT-SRM

*: 119 EU + 1 EFTA labs submitting results

Coverage

≥ 80 %	25-49 %
50-79 %	<25 %

EURL-SRM

FALSE NEGATIVES

False Negatives, COMPULSORY COMPOUNDS = 9

EU+EFTA

	Compound	MRRL [mg/kg]	Assigned Value [mg/kg]	No. FNs	Lab Code	RL [mg/kg]
COMPULSORY	Cyromazine	0.01	1.512	2	83	0.01
					43	0.01
	DTCs	0.03	1.297	2	55	0.03
					77	0.3
	TFNA	0.01	0.756	1	114	0.03
	Tolylfluanid	0.01	*0.598*	4	19 (NRL)	0.01
					35 (NRL)	0.01
					70	0.01
					96 (NRL)	0.005

EURL-SRM

FALSE NEGATIVES

False Negatives, OPTIONAL COMPOUNDS = 20

EU+EFTA

	Compound	MRRL [mg/kg]	AV [mg/kg]	No. FNs	Lab Code	RL [mg/kg]
OPTIONAL	Chlorate	0.02	2.033	3	18	0.01
					49	0.02
					107	0.1
	Dithianon	0.01	*1.729*	3	7 (NRL)	0.01
					88	0.01
					107	0.01
	Perchlorate	0.02	0.260	2	18	0.01
					49	0.02
	Phosphonic acid	0.05	9.831	2	5	<0.01
					43	0.01
	Pymetrozine	0.01	*0.432*	2	49	0.01
					96 (NRL)	0.005
	Quizalofop	0.01	0.171	6	4	0.01
					14	0.01
					32	0.01
					81	0.01
					91	0.01
					98	0.01
	Triclopyr	0.01	0.177	2	14	0.01
					118	0.01

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FALSE POSITIVES

EU+EFTA

False Positives (FP) = 3

	Compound	MRRL [mg/kg]	No. of FP	Lab Code	RL [mg/kg]	Results [mg/kg]
COMPULSORY	Ethephon	0.02	2	88	0.01	0.131
				102	0.05	1.2
	Glyphosate	0.03	1	88	0.01	0.03

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RECOVERY CORRECTION APPROACHES

Approaches employed for „Recovery Correction“
ILIS
Procedural Calibration
Procedural Calibration + ILIS
Recovery Factor
Recovery Factor + ILIS
Standard Addition to Sample Portions
Standard Addition to Sample Portions + ILIS
Standard Addition to Extract Aliquots + ILIS

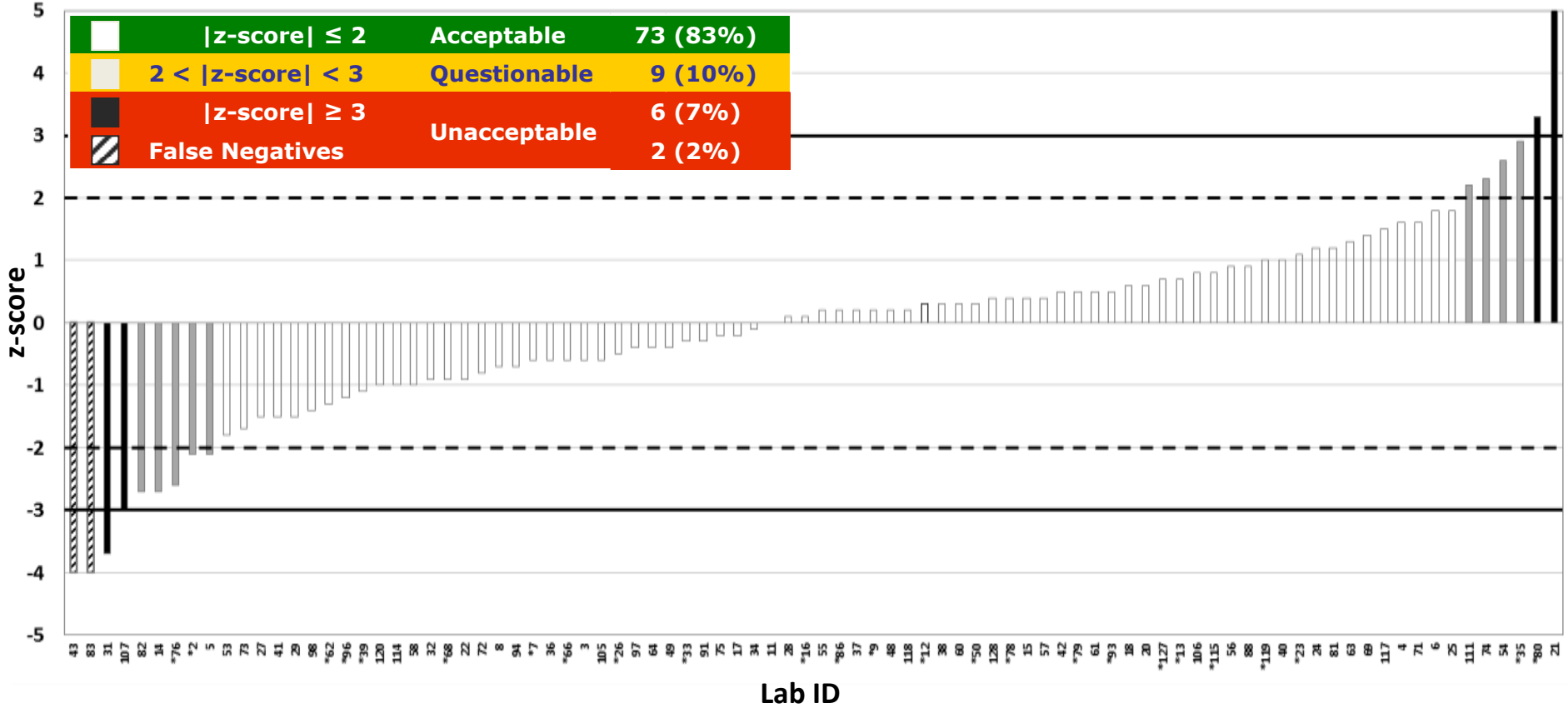
Sum>100 due to overlap of approaches

Labs having corrected for recovery using various approaches

Compound	ILIS	Proce-dural	Std Add to sample portions	Recov. factor	Std Add to extr. aliquots	None	No data
BAC-C14	**2%**	10%	**26%**	2%	8%	**48%**	6%
Chlorate	**49%**	13%	16%	-	13%	17%	11%
Cyromazine	14%	16%	**17%**	7%	14%	**31%**	6%
Dithianon	7%	**19%**	**19%**	2%	12%	**24%**	21%
Dithiocarbamates	3%	**13%**	10%	3%	2%	**59%**	9%
Dodine	-	10%	**19%**	5%	10%	**48%**	8%
Perchlorate	**49**	13%	21%	-	11%	19%	9%
Phosphonic acid	**44**	17%	22%	-	7%	20%	10%
Pymetrozine	-	14%	**20%**	6%	11%	**41%**	16%
Quizalofop	-	13%	**20%**	2%	7%	**43%**	15%
TFNA	-	12%	**20%**	2%	15%	**42%**	9%
TFNG	-	11%	**20%**	2%	15%	**44%**	8%
Tolylfluanid	-	10%	**22%**	2%	13%	**42%**	11%
Triclopyr	-	11%	**18%**	2%	11%	**46%**	11%

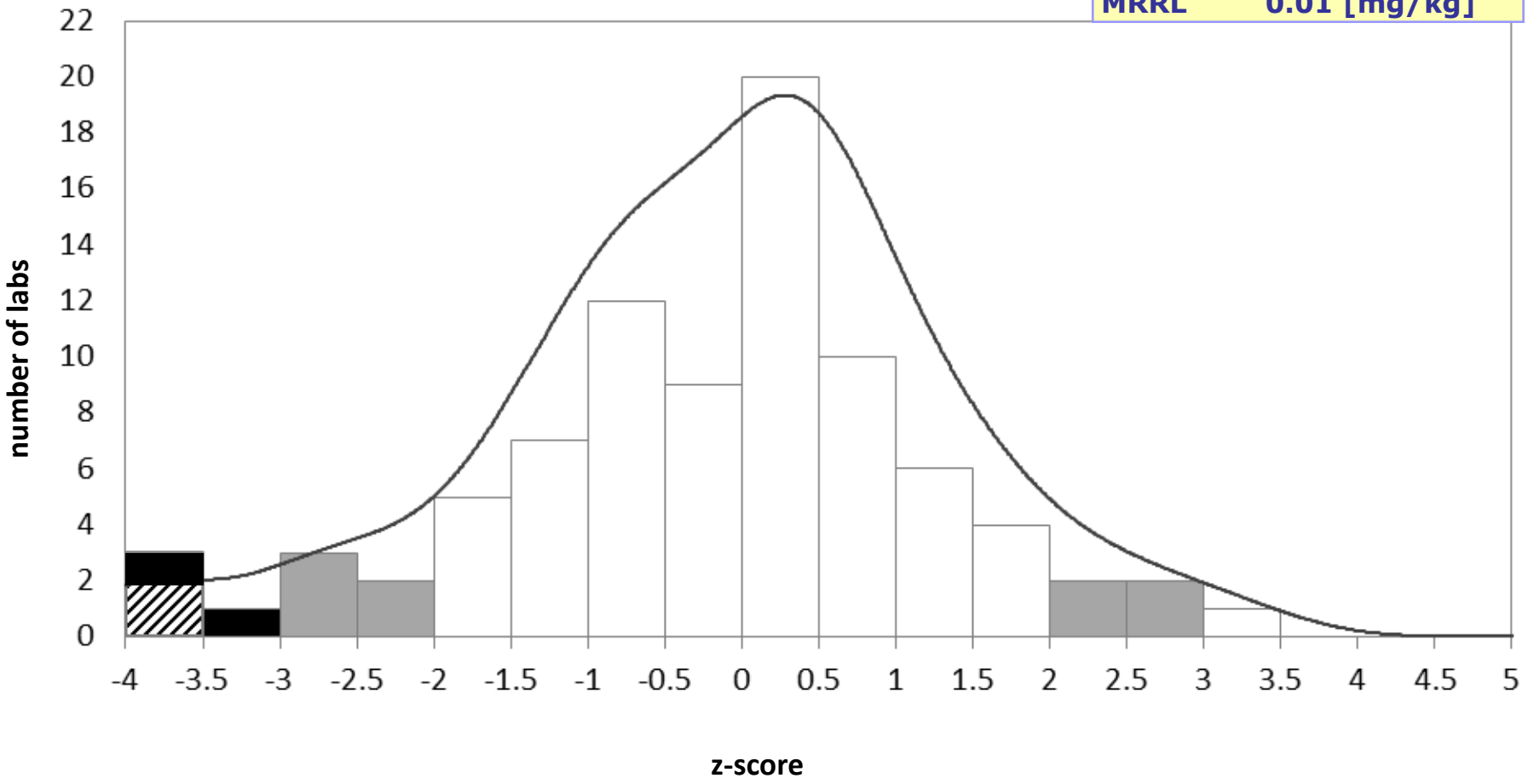
Cyromazine

Results	86
False Neg.	2
AV	1.512 [mg/kg]
CV*	31.8 %
MRRL	0.01 [mg/kg]



Cyromazine

Results	86
False Neg.	2
AV	1.512 [mg/kg]
CV*	31.8 %
MRRL	0.01 [mg/kg]



Results	86
False Neg.	2
AV	1.512 [mg/kg]
CV*	31.8 %
MRRL	0.01 [mg/kg]

CYROMAZINE

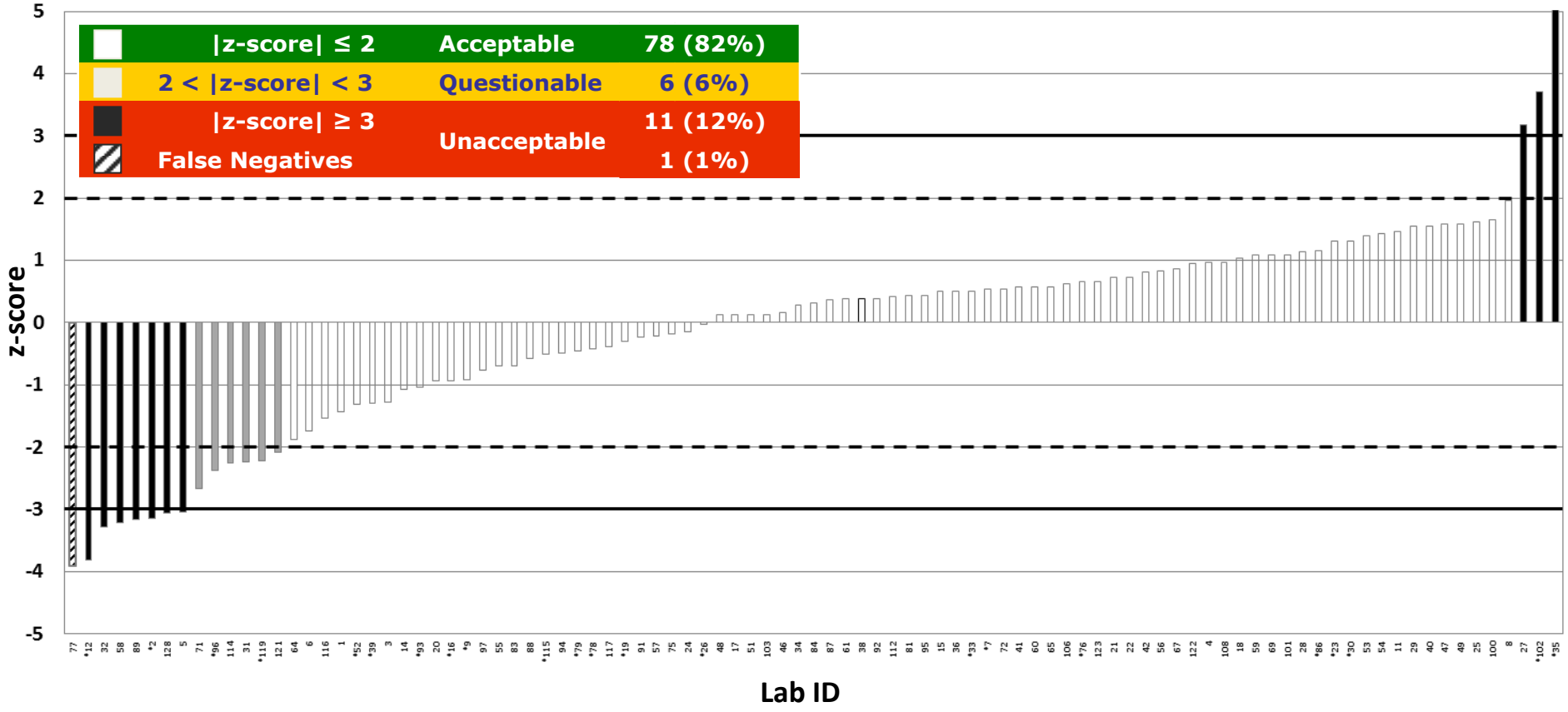
	ALL	Recov. Corr. applied		No Recov. Corr.
		All	ILIS	
No. of Results	86	43	13	39
Robust Mean	1.512	1.672	1.647	1.306
CV*	32 %	26 %	19 %	42 %
Distance to AV	**0 %**	+ 11%	+9%	- 14 %
Distance to Robust Mean of Rec. Corr. results		**0 %**		-22 %

Approach applied to correct for recovery	ILIS	Procedural	Standard Addition to Sample Portions	Recovery Factor
No. of labs	13	14	15	6
Note: Several labs have employed combinations				

DITHIOCARBAMATES (EXPRESSED AS CS2)

DITHIOCARBAMATES

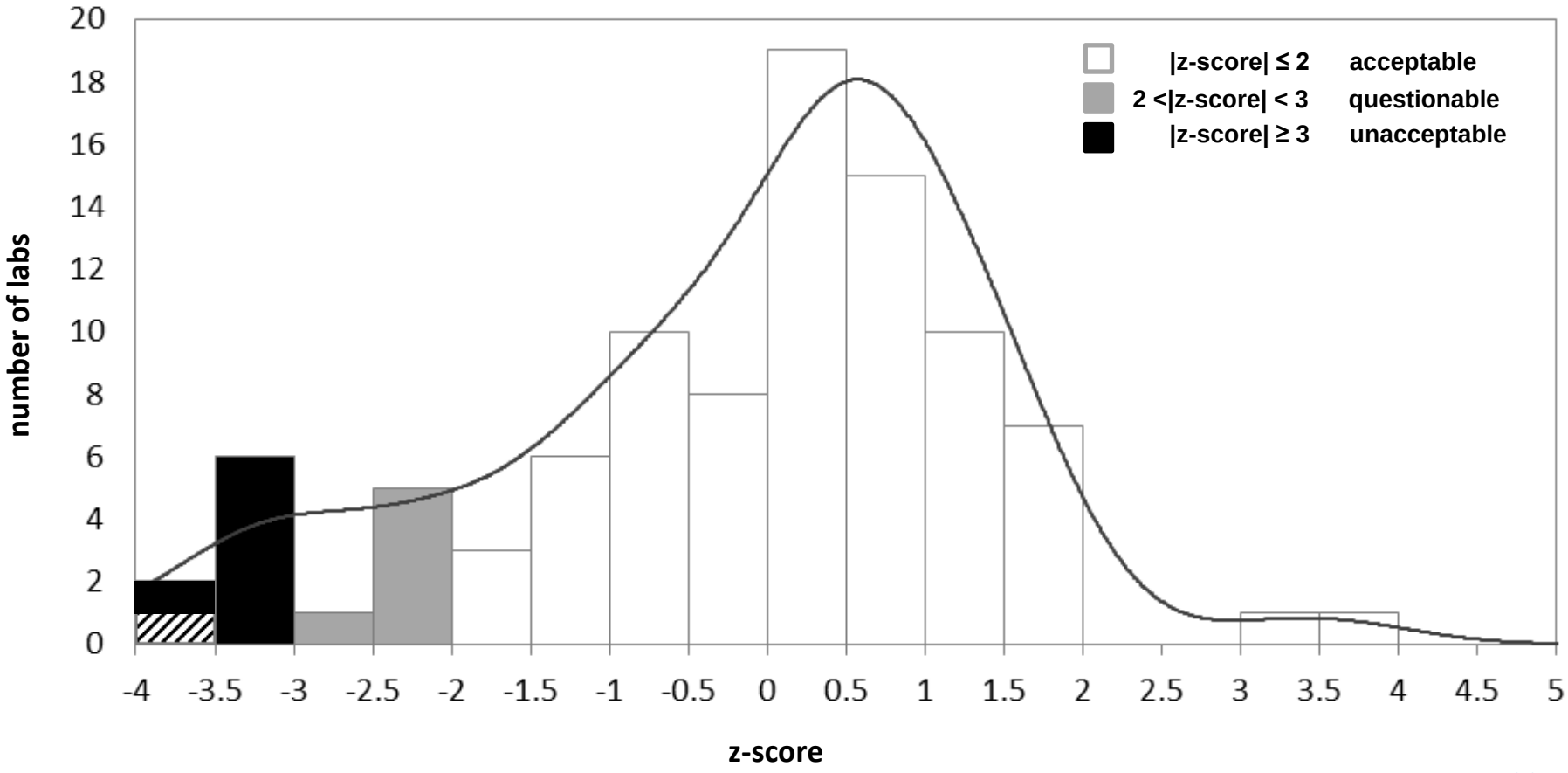
Results	94
False Neg.	1
AV	1.292 [mg/kg]
CV*	34.6 %
MRRL	0.03 [mg/kg]



DITHIOCARBAMATES (EXPRESSED AS CS2)

DITHIOCARBAMATES

Results	94
False Neg.	1
AV	1.292 [mg/kg]
CV*	34.6 %
MRRL	0.03 [mg/kg]



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DITHIOCARBAMATES (EXPRESSED AS CS2)

DITHIOCARBAMATES

Results	94
False Neg.	1
AV	1.292 [mg/kg]
CV*	34.6 %
MRRL	0.03 [mg/kg]

	No. of results	FNs	Robust Mean [mg/kg]	CV*	AAZ
All	94	1	1.292	34.6%	1.197
Liq.-liq-Partitioning	43	2	1.317	40.5%	1.356
Headspace	22		1.109	54.5%	1.355
Spectrophotometric	22		1.413	16.6%	0.718

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TRENDS IN DTC-ANALYSIS OVER THE YEARS

		Liq.-liq-Partitioning	Headspace	Spectrophotometric
SRM6	No of Results	26	12	24
	Robust Mean	0.619	0.531	0.601
	CV	27.9%	44.4%	21.0%
	AAZ	0.89	1.11	0.63
SRM7	No of Results	31	16	32
	Robust Mean	0.663	0.660	0.571
	CV	27.8%	25.8%	20.6%
	AAZ	1.04	1.03	0.59
SRM10	No of Results	32	27	22
	Robust Mean	0.659	0.525	0.543
	CV	35.5%	44.1%	18.5%
	AAZ	1.38	1.36	0.63
SRM11	No of Results	43	22	22
	Robust Mean	1.317	1.109	1.413
	CV	40.5%	54.5%	16.6%
	AAZ	1.36	1.36	0.72
AVG	CV	33%	43%	19%

Reaction time in shaking water bath
Impact on DTCs as CS2 results (isooctane method)

Using Spinach homogenate of EUPT-SRM11

Relative Results of DTCs as CS2

80°C / 1h ➔ 71% (RSD high)

80°C / 2h ➔ 83%

80°C / 3h ➔ 95%

80°C / 4h ➔ **100% (set)**

More experiments on impact of temperature and reagent concentration will follow

Reaction Temperature and Time (ALL METHODS)

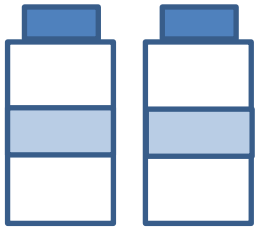
Reaction Temp. °C	No. of labs	Reaction Time (min)
50	1	80 min
65	1	120 min
70	7	60 min (1x), **120 min (5x),** 150 min (1x)
80	**48**	20 min (1x), 30 min (2x), **45 min (5x), 60 min (16x),** 90 min (1x), **120 min (22x)**
90	**11**	30 min (2x), **60 min (6x),** 90 min (2x), 120 min (1x)
100	**17**	**30 min (10x),** 35 min (1x), 45 min (1x), **60 min (5x)**
180	1	60 min
200	1	60 min

For LLP (isooctane method) - Average concentration reported

80°C **60 min** : 1.26 mg/kg (N=10)

80°C **120 min**: 1.40 mg/kg (N=15)

} Small populations thus only indicative



PT-Material from 2 bottles

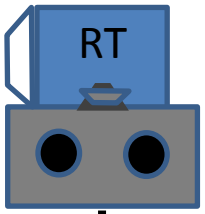
Finely chopped with ceramic knife

Transferred to PLASTIC bowl, mixed well

ANALYSIS Set at 100%

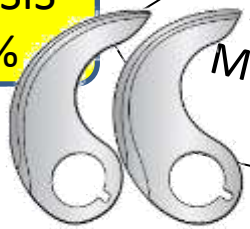
Left to **defrost** overnight (16h)

Transferred to KNIFE MILL + mixed 10 min



ANALYSIS 90%

Stirred with METAL KNIVES 10 min



ANALYSIS 101%

Stirred with PLASTIC SPOON 10 min

ANALYSIS 102%

Transfered to metal bowl and agitated 10 min

ANALYSIS 98%

Overall <u>little impact</u> of defrosting or metal contact on DTCs as CS2 results

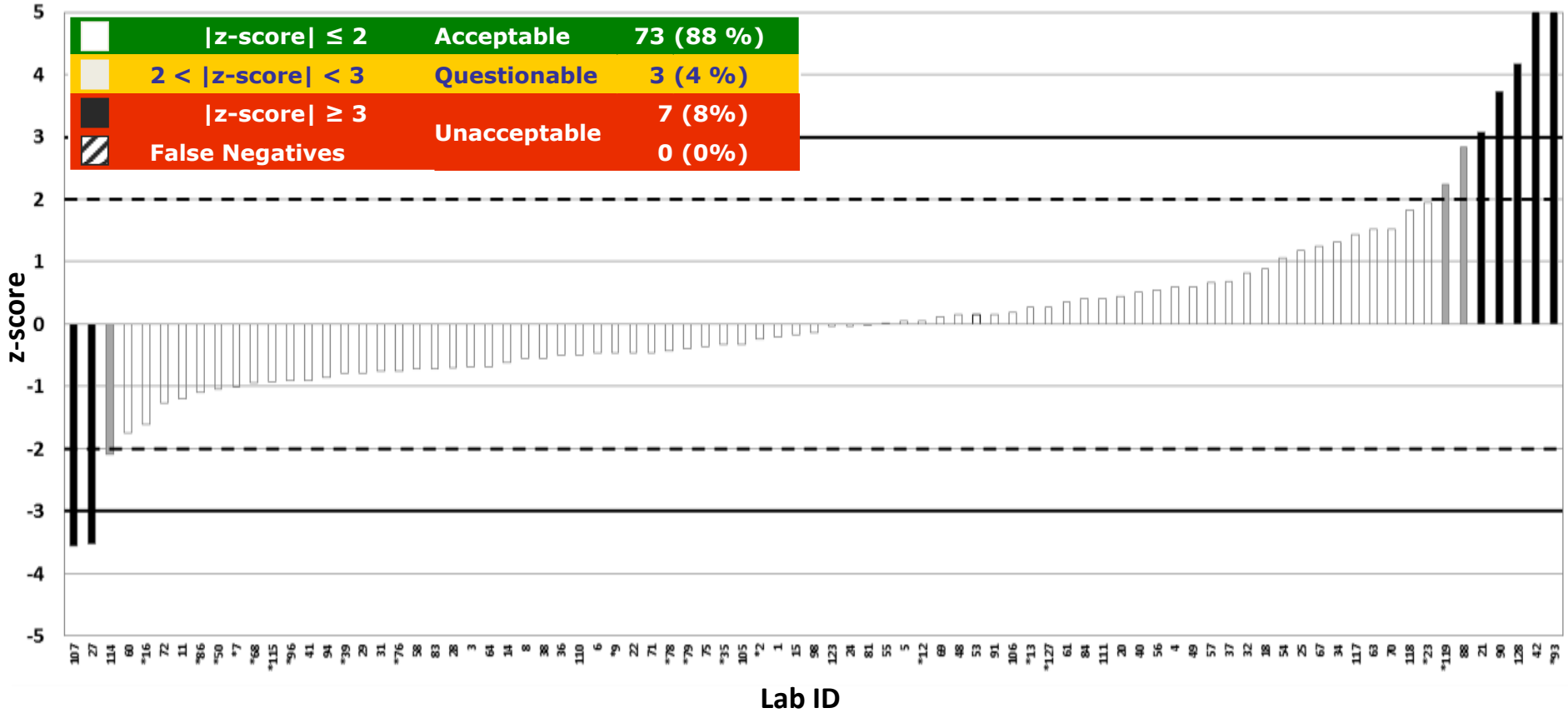
Feedback from an OfL

Lettuce with Incurred DTCs
Repetitive thawing at RT + Stiring with Metal spoon before analysis

Day	Determined conc. DTC [mg/kg]
Day 0	3.04
Day 5	3.12 (after 4h at RT ➔ 2.95)
Day 11	2.86
Day 18	2.88

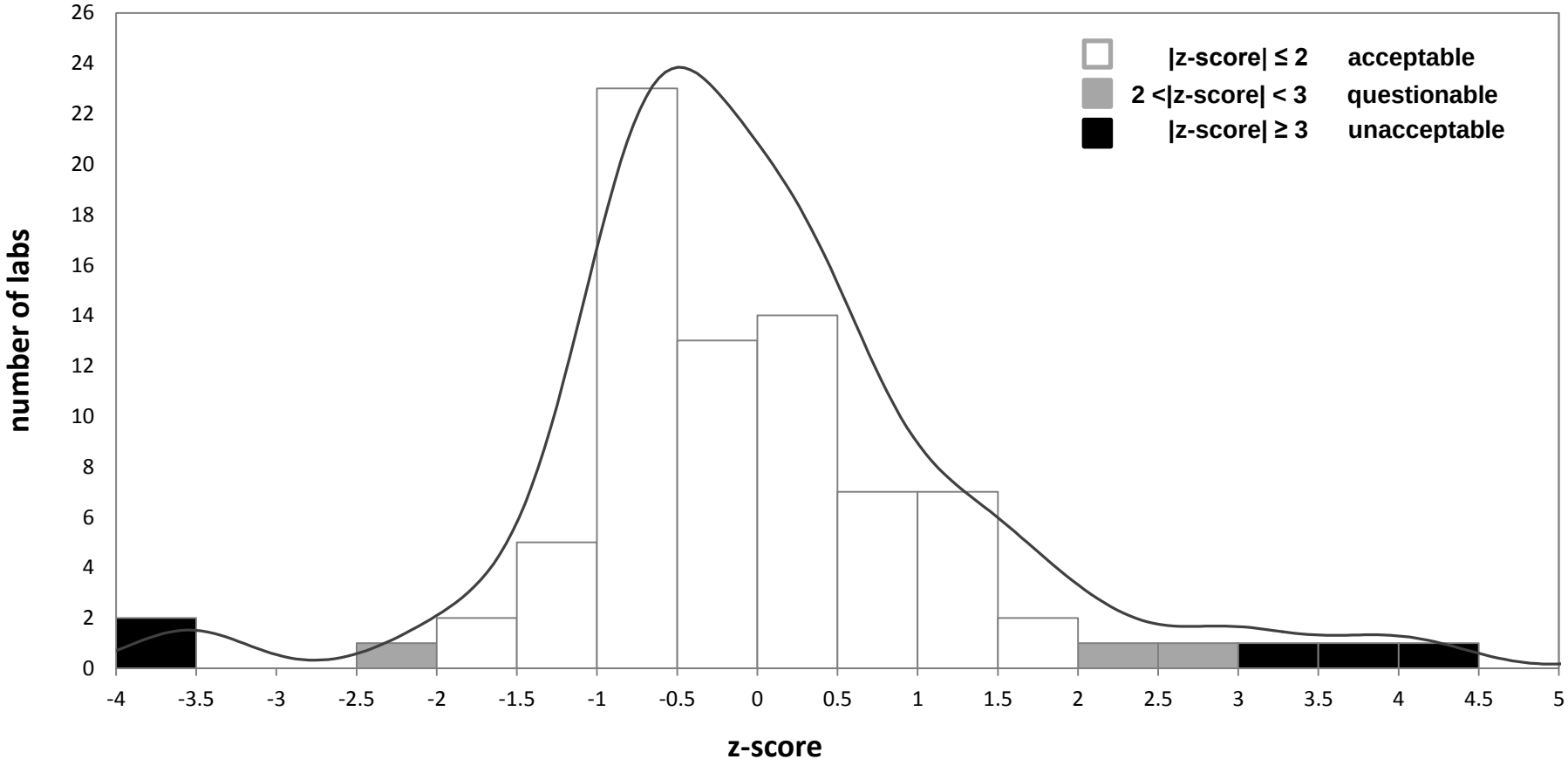
DODINE

Results	83
False Neg.	0
AV	1.243 [mg/kg]
CV*	26.2 %
MRRL	0.01 [mg/kg]



DODINE

Results	83
False Neg.	0
AV	1.243 [mg/kg]
CV*	26.2 %
MRRL	0.01 [mg/kg]



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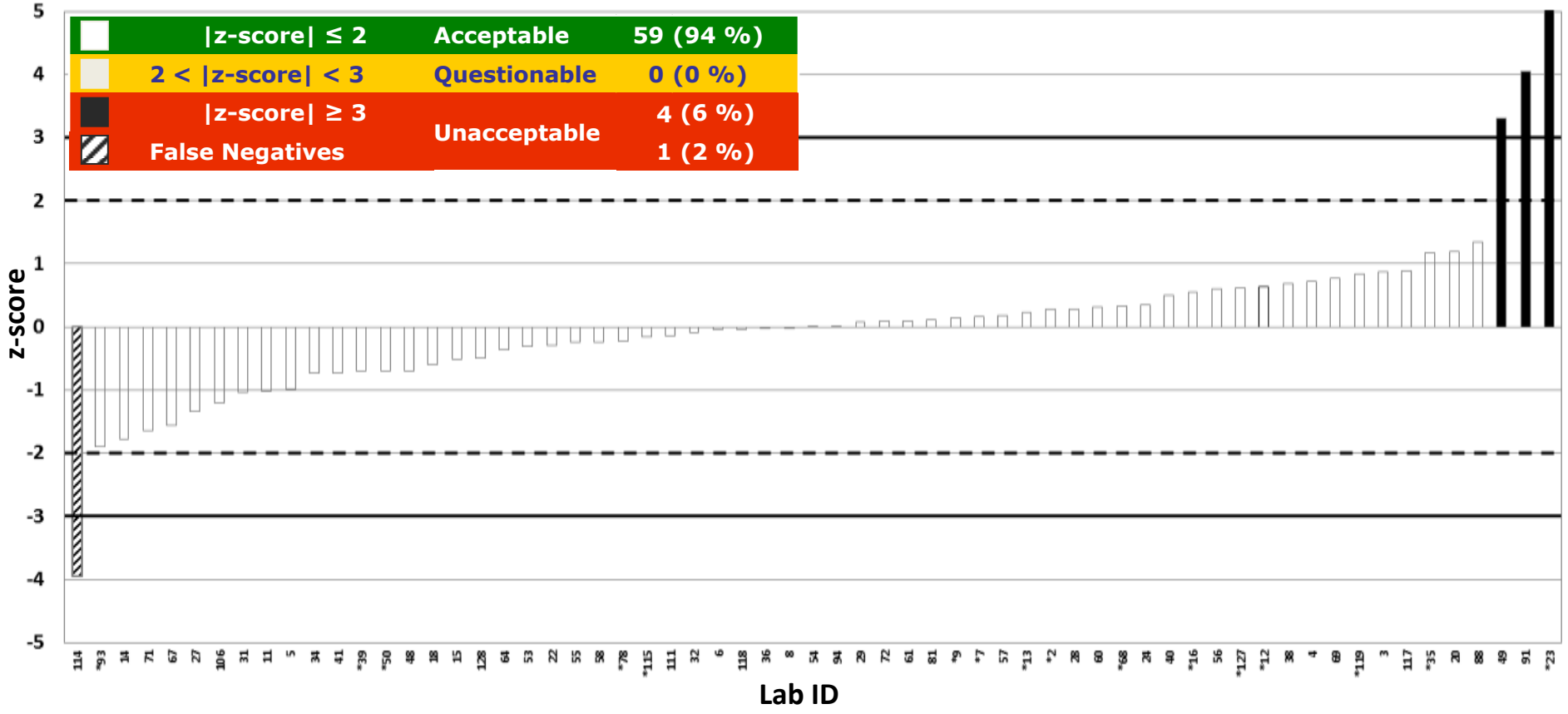
TFNA (METABOLITE OF FLONICAMID)

TFNA

Results	62
False Neg.	1
AV	0.756 [mg/kg]
CV*	20.0 %
MRRL	0.01 [mg/kg]

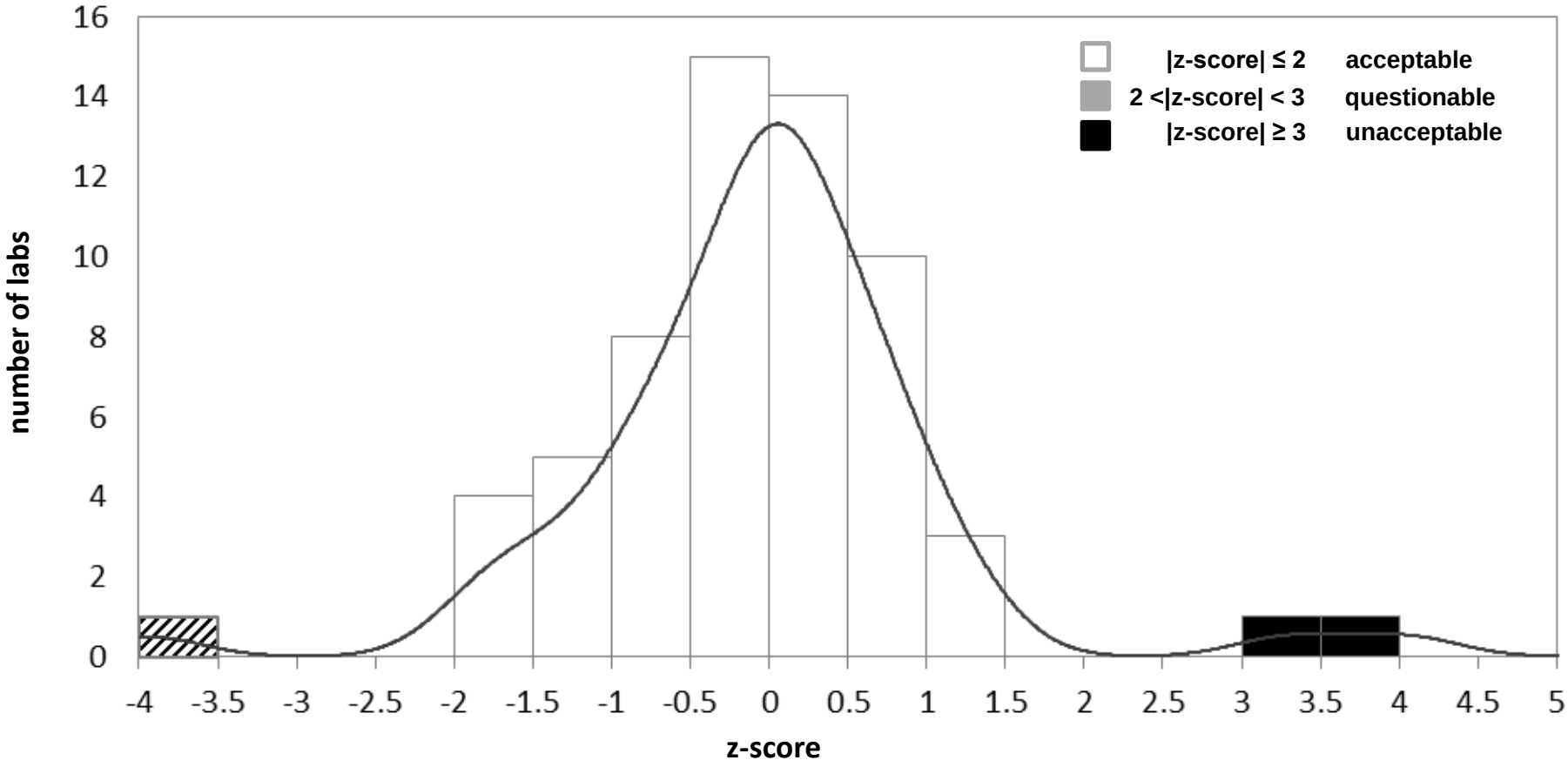


EURL-SRM

TFNA (METABOLITE OF FLONICAMID)

TFNA

Results	62
False Neg.	1
AV	0.756 [mg/kg]
CV*	20.0 %
MRRL	0.01 [mg/kg]

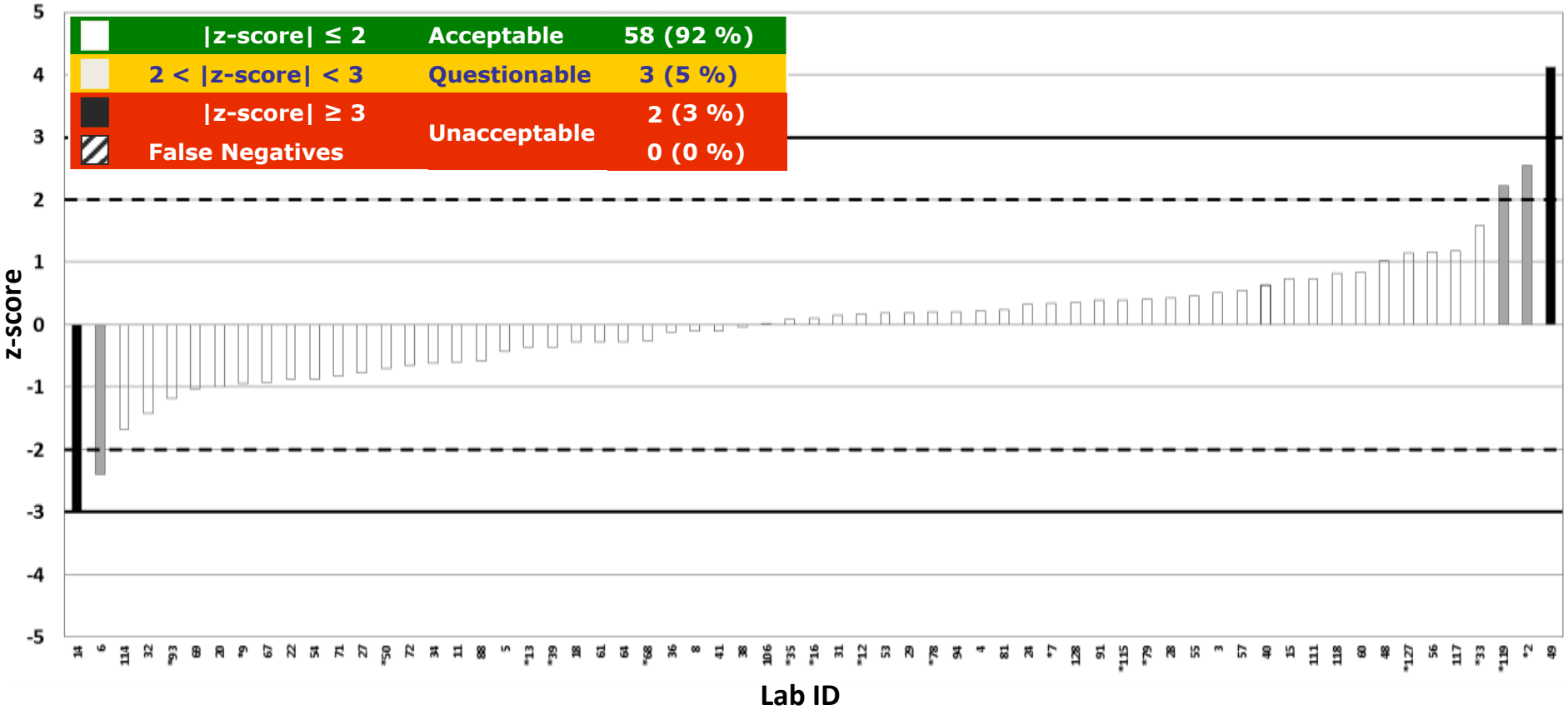


EURL-SRM

TFNG (METABOLITE OF FLONICAMID)

TFNG

Results	63
False Neg.	0
AV	0.448 [mg/kg]
CV*	20.7 %
MRRL	0.01 [mg/kg]

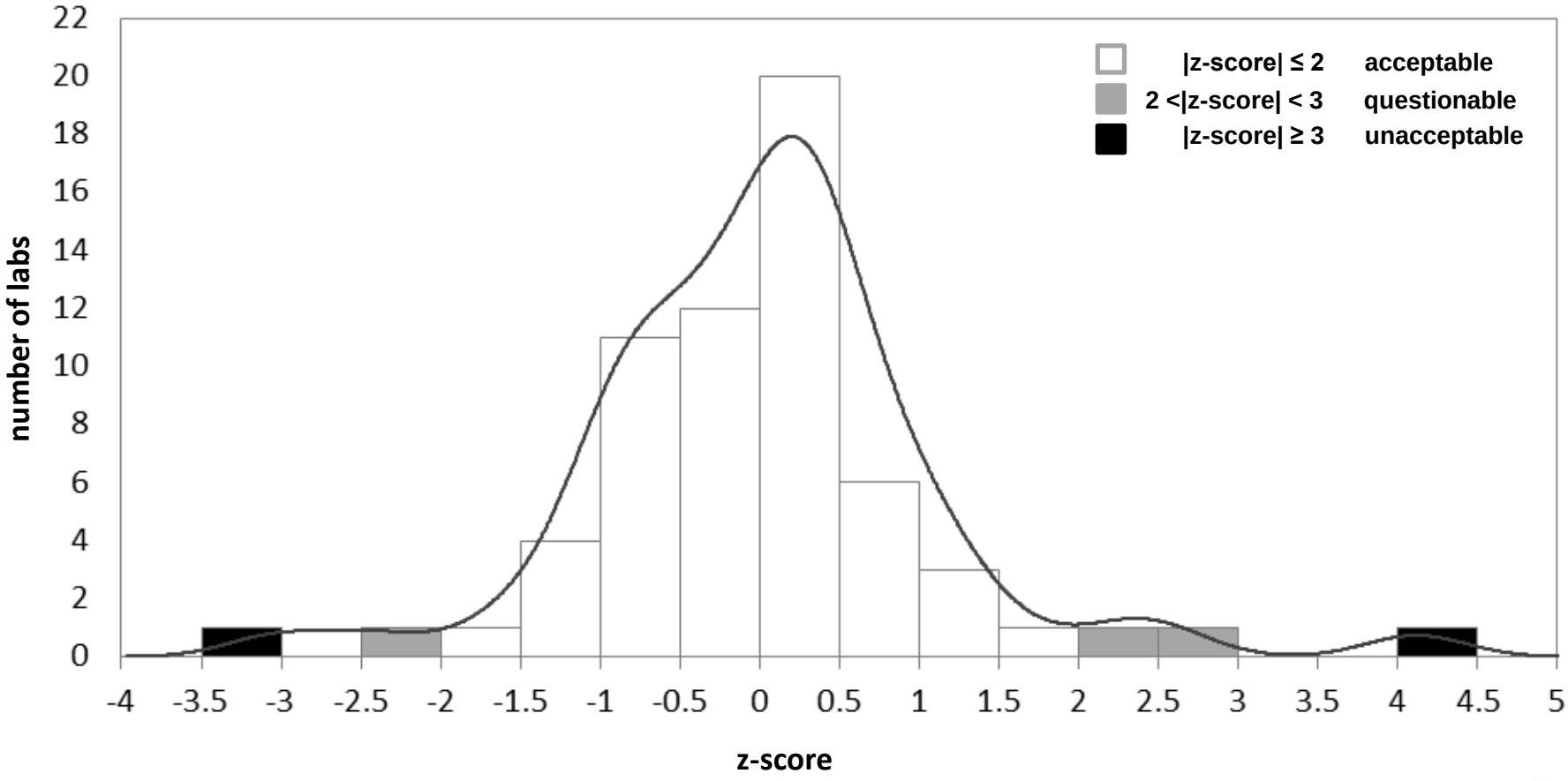


EURL-SRM

TFNG (METABOLITE OF FLONICAMID)

TFNG

Results	63
False Neg.	0
AV	0.448 [mg/kg]
CV*	20.7 %
MRRL	0.01 [mg/kg]



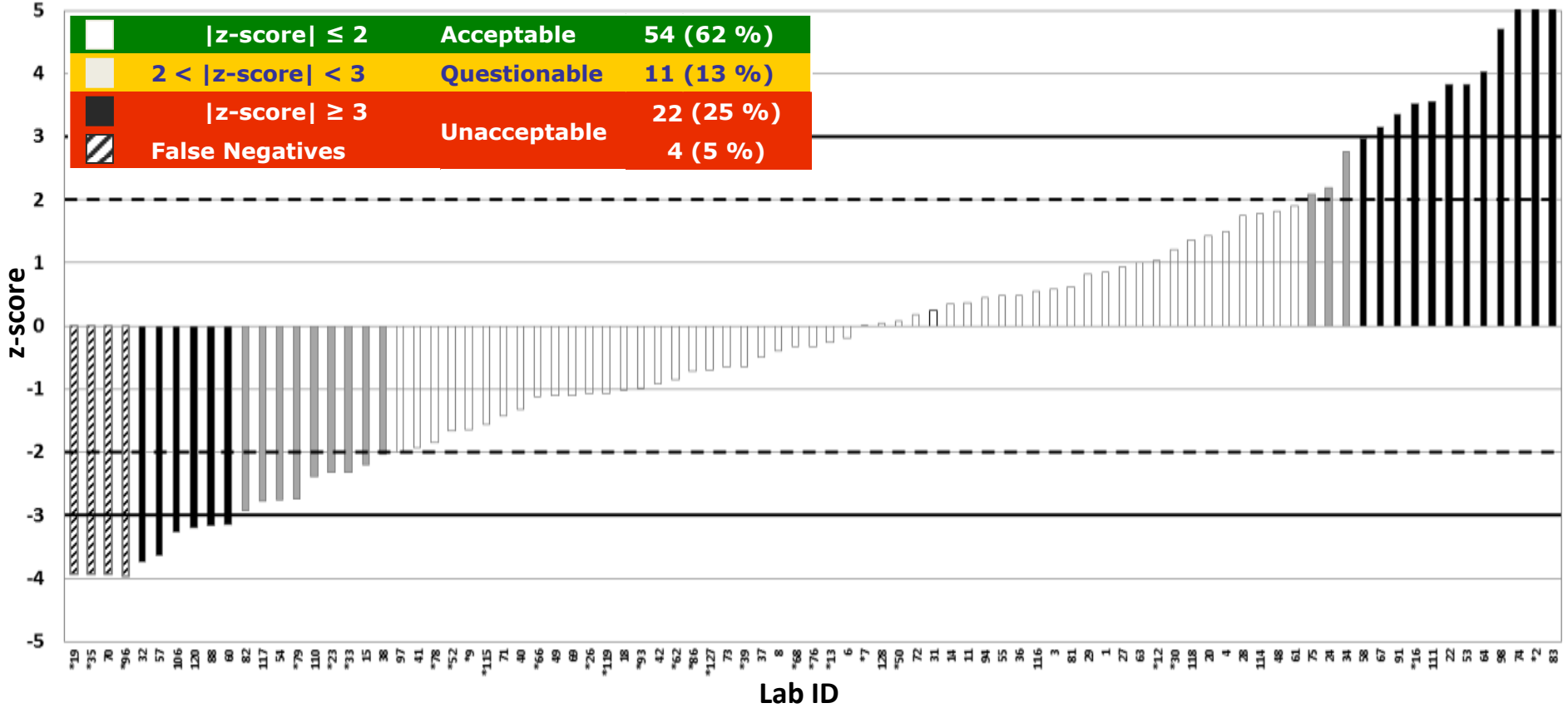
EURL-SRM

TOLYLFLUANID (PARENT ONLY)

TOLYLFLUANID

FOR INFORMATIVE PURPOSE ONLY

Results	83
False Neg.	4
AV	0.598 [mg/kg]
CV*	57.5 %
MRRL	0.01 [mg/kg]



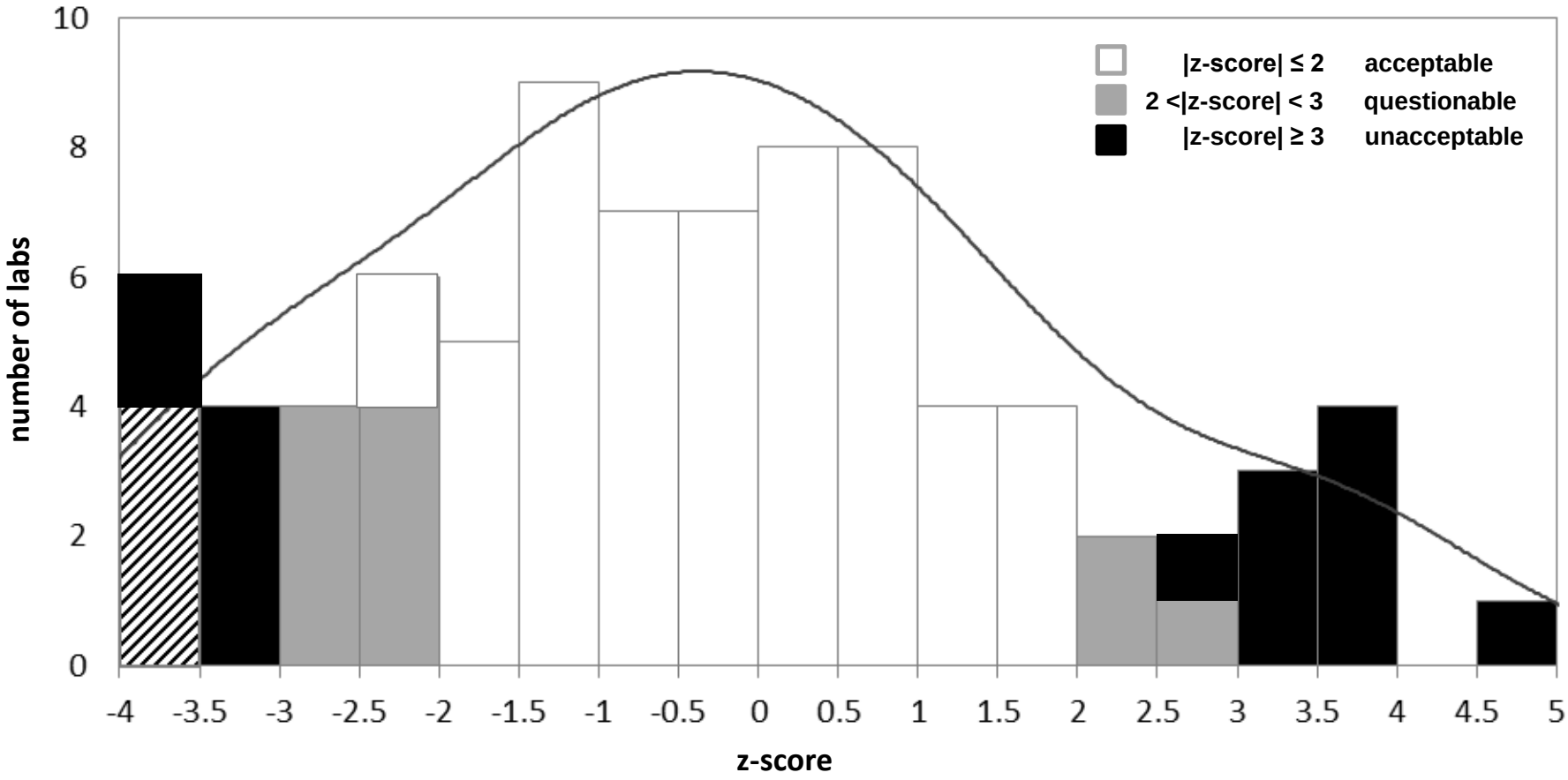
EURL-SRM

TOLYLFLUANID (PARENT ONLY)

TOLYLFLUANID

FOR INFORMATIVE PURPOSE ONLY

Results	83
False Neg.	4
AV	0.598 [mg/kg]
CV*	57.5 %
MRRL	0.01 [mg/kg]



TOLYLFLUANID

FOR INFORMATIVE PURPOSE ONLY

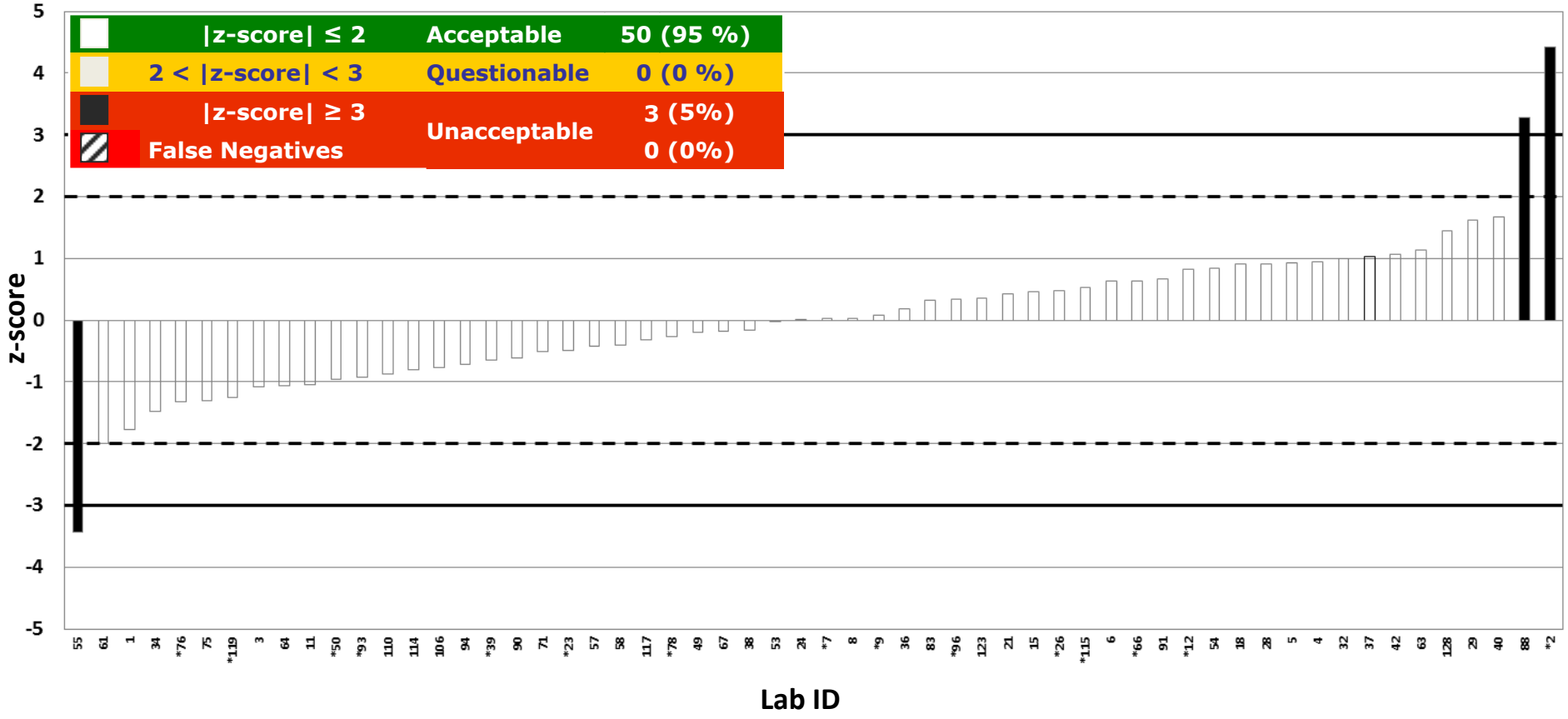
Results	83
False Neg.	4
AV	0.598 [mg/kg]
CV*	57.5 %
MRRL	0.01 [mg/kg]

	No Results	AlgA-Mean	CV*
ALL	83	**0.598**	57.5%
Ambient (initial sample Temp.)	20	0.523	60.4%
FA-QuEChERS (with formic acid)	14	0.607	26.9%
Deep Frozen (initial sample Temp.)	16	**0.813**	37.3%

BAC-C14 (EXPRESSED AS CHLORIDE SALT)

BAC-C14

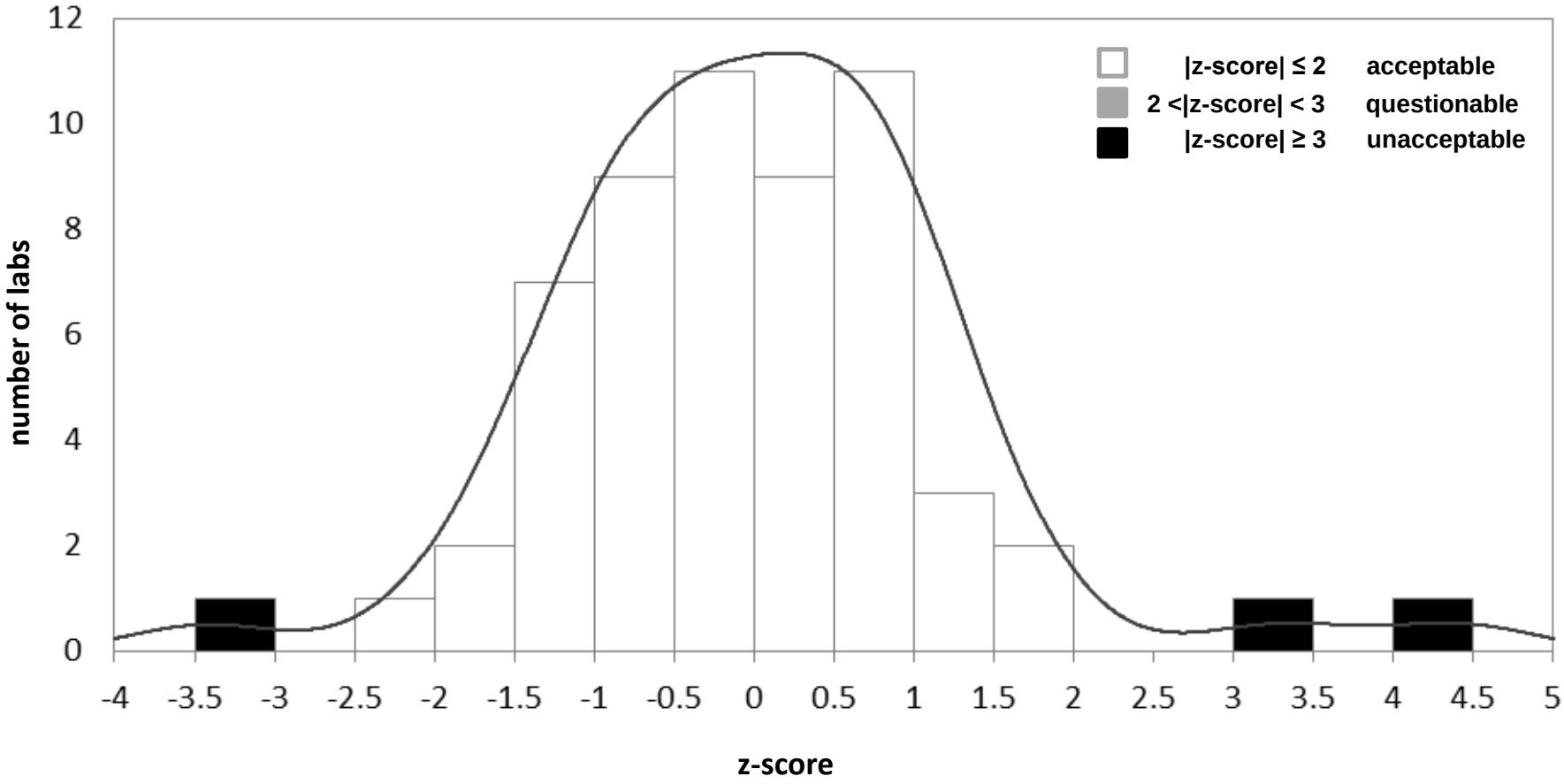
Results	58
False Neg.	0
AV	0.285 [mg/kg]
CV*	25.8 %
MRRL	0.02 [mg/kg]



BAC-C14 (EXPRESSED AS CHLORIDE SALT)

BAC-C14

Results	58
False Neg.	0
AV	0.285 [mg/kg]
CV*	25.8 %
MRRL	0.02 [mg/kg]

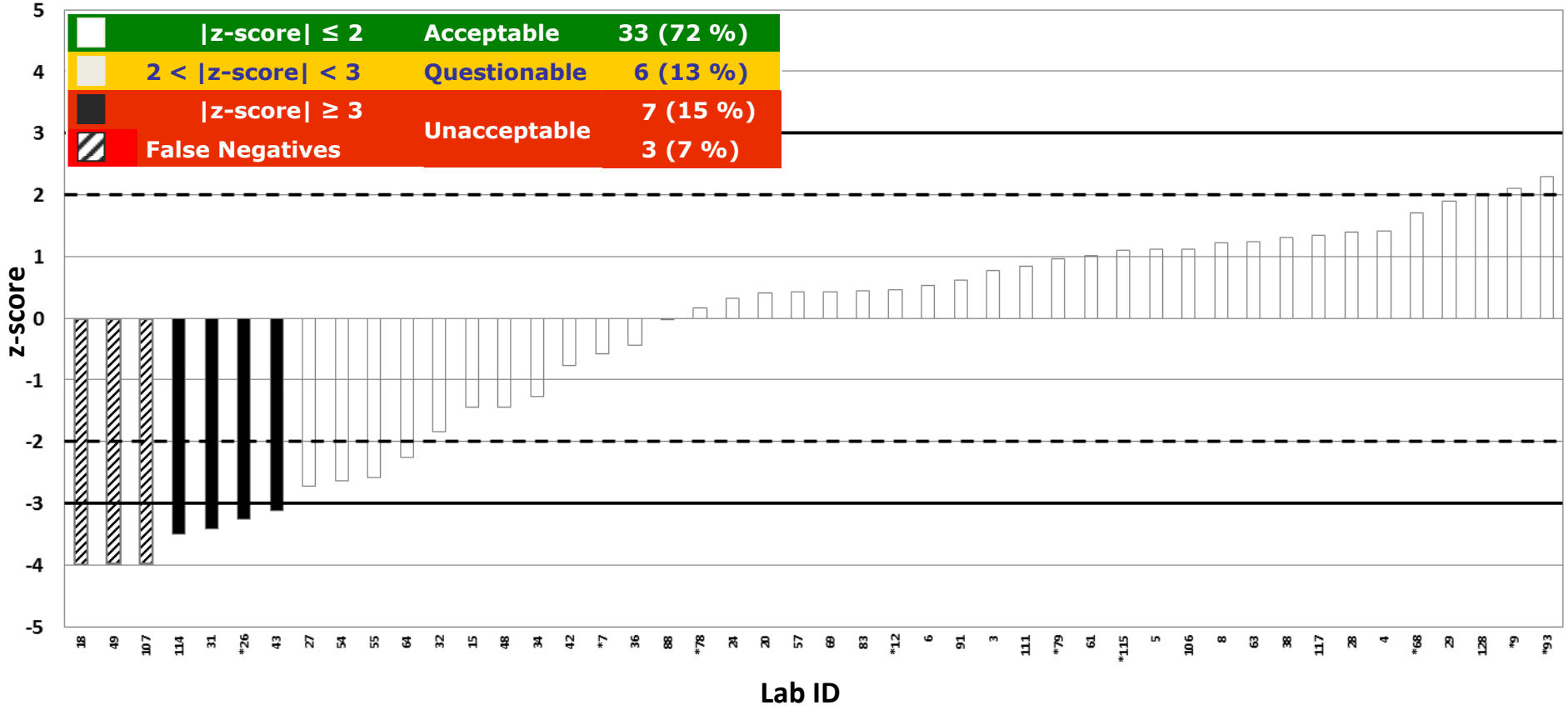


CHLORATE (ANION)

CHLORATE

FOR INFORMATIVE PURPOSE ONLY

Results	43
False Neg.	3
AV	2.03 [mg/kg]
CV*	44.6 %
MRRL	0.02 [mg/kg]

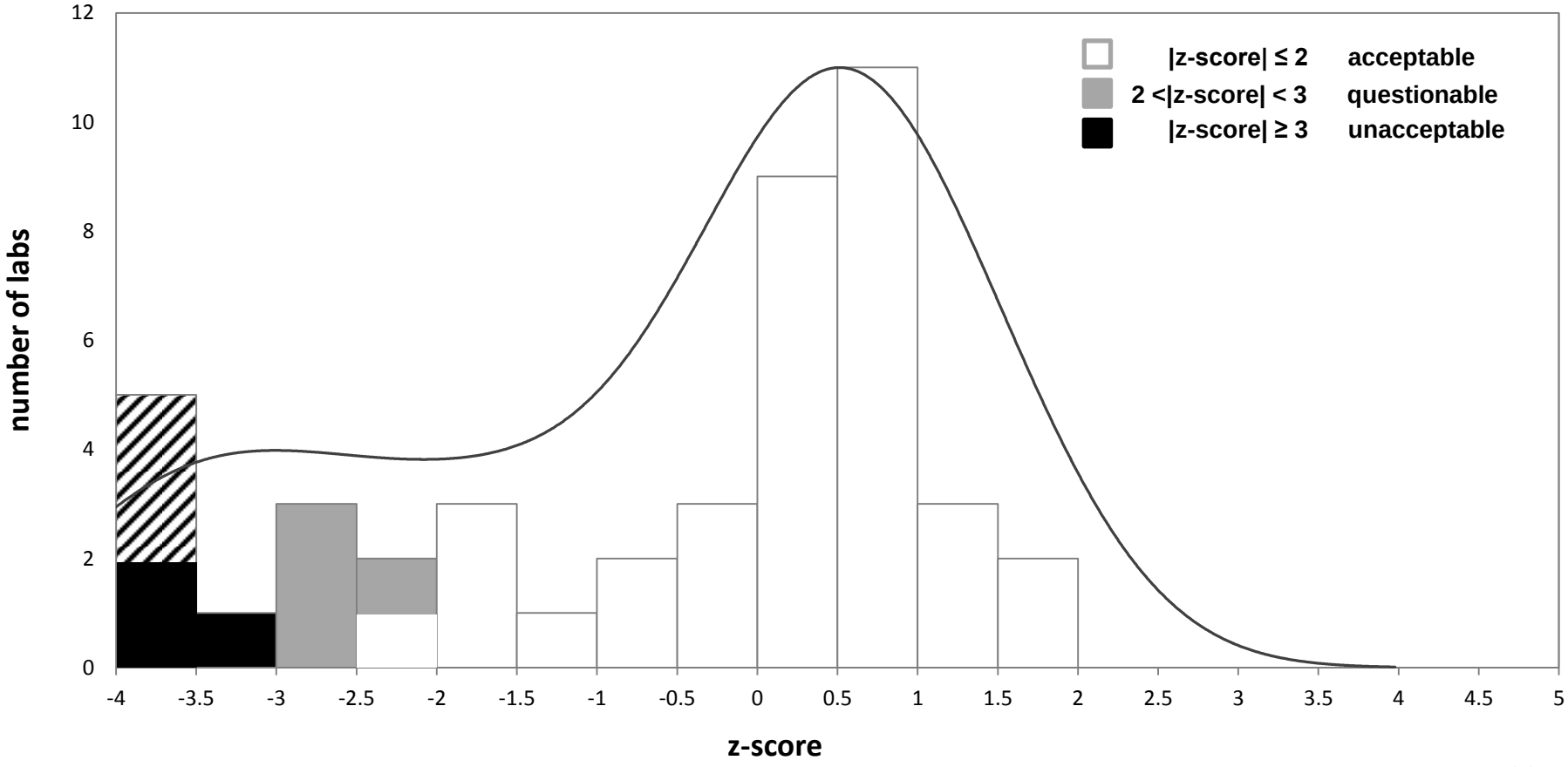


CHLORATE (ANION)

CHLORATE

FOR INFORMATIVE PURPOSE ONLY

Results	43
False Neg.	3
AV	2.03 [mg/kg]
CV*	44.6 %
MRRL	0.02 [mg/kg]



CHLORATE

FOR INFORMATIVE PURPOSE ONLY

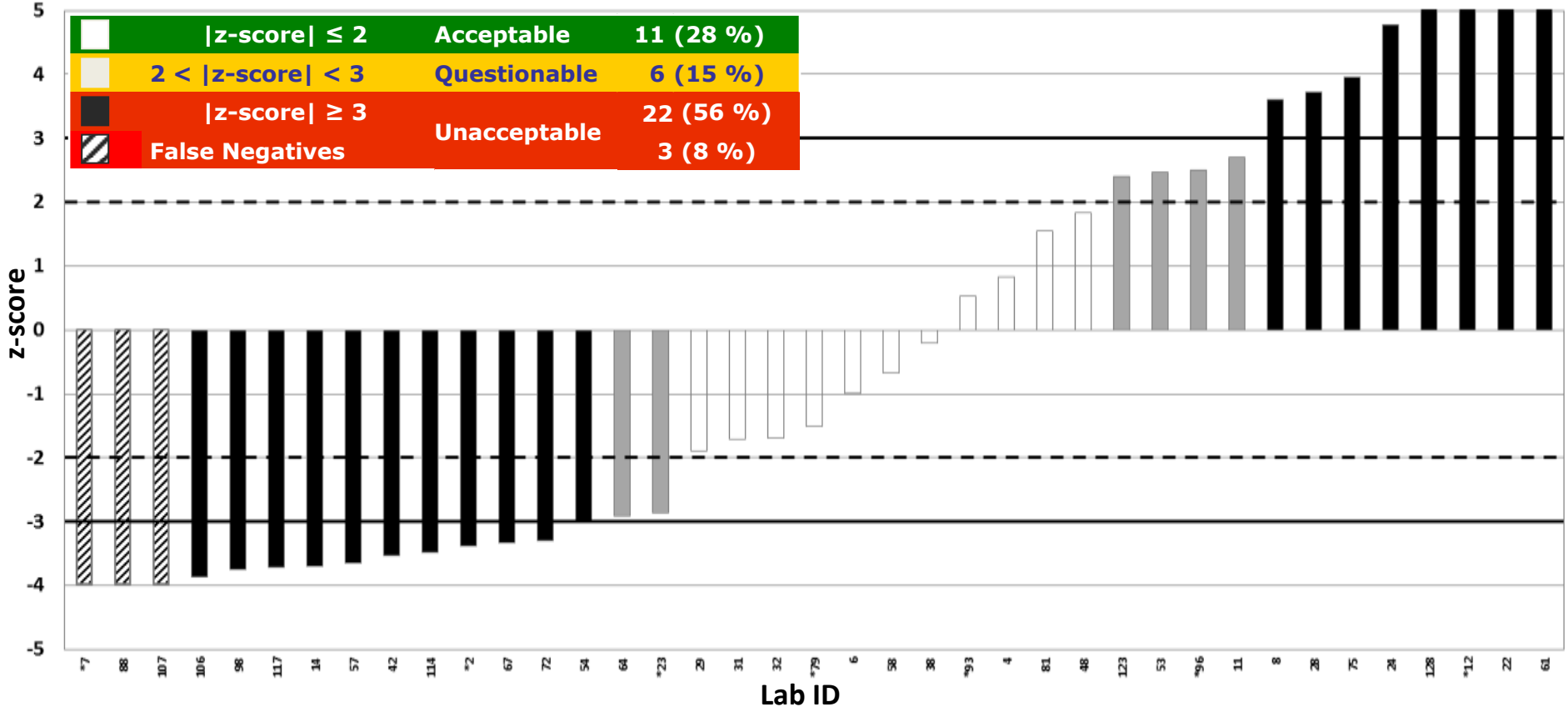
Results	43
False Neg.	3
AV	2.03 [mg/kg]
CV*	44.6 %
MRRL	0.02 [mg/kg]

	ALL	Using ILIS	Not using ILIS
Number of Results	43	22	23
Robust Mean	2.03	2.47	1.61
CV*	**45%**	**16%**	**67%**
Vesus AV	**0 %**	+ 22 %	- 21 %
Versus Rec. Corr.	-18%	**0 %**	-35 %

DITHIANON

(NO CALUCULATION OF Z-SCORE)

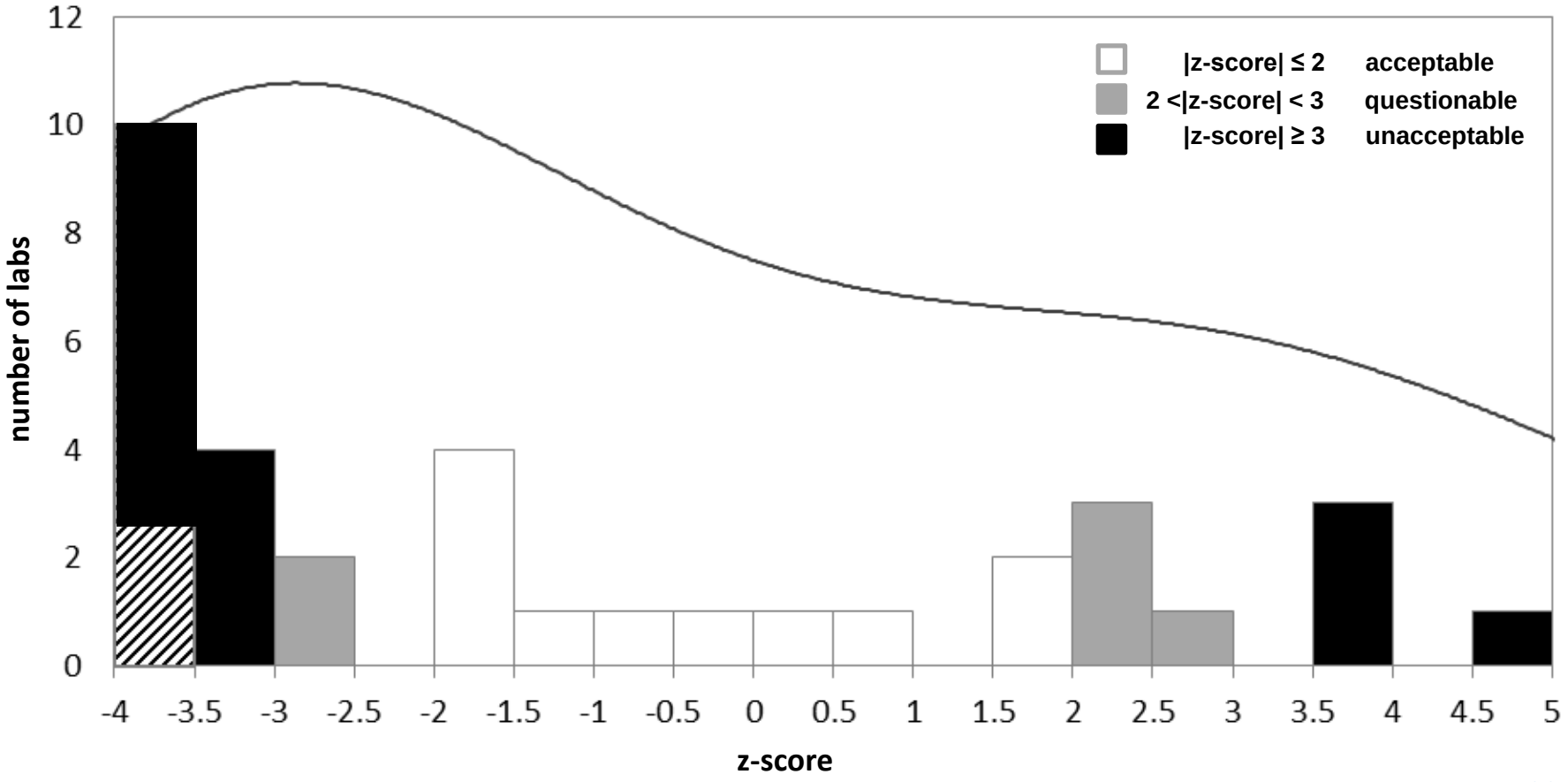
Results	36
False Neg.	3
AV	1.729 [mg/kg]
CV*	94.3 %
MRRL	0.01 [mg/kg]



DITHIANON

(NO CALUCULATION OF Z-SCORE)

Results	36
False Neg.	3
AV	1.729 [mg/kg]
CV*	94.3 %
MRRL	0.01 [mg/kg]



DITHIANON

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

EURL-SRM - Analytical Observations Report

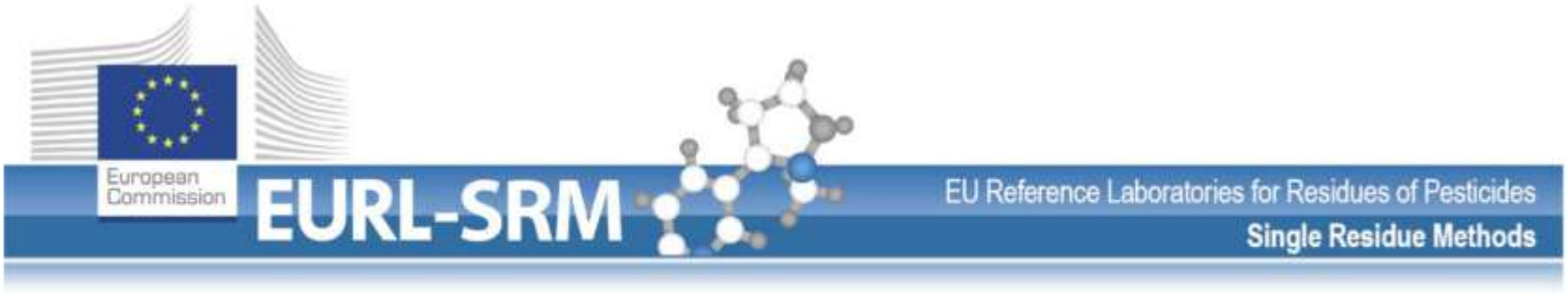
concerning the following...

- **Compound(s)**: Dithianon, Dithianon D4
- **Commodities**: Fruit and vegetables, cereals
- **Extraction Method(s)**: QuEChERS, QuEChERS (variations)
- **Instrumental analysis**: LC-MS/MS, ESI (neg.)

Analysis of Dithianon by the QuEChERS Method - Impact of pH on recovery rates

Version 2.1 (last update: 09.05.2016)

DITHIANON



EURL-SRM – Analytical Method Report

Analysis of Dithianon in Food of Plant Origin using acidified QuEChERS and LC-MS/MS

Version 2 (last update: 29.04.16)

DITHIANON

Tab. 4: Recovery data for Dithianon from various commodities:

Matrix Type	Matrix	Spiking Level	IS	QuEChERS			QuEChERS + 4 % HAc			QuEChERS + 1 % FA			QuEChERS + 1 % SA		
				n	Mean Rec.%	RSD %	n	Mean Rec.%	RSD %	n	Mean Rec.%	RSD %	n	Mean Rec.%	RSD %
High water	Lettuce	0.1	BNPU	3	22	13.7	3	46	12.7	5	76	3.2	5	90	4.1
	Cucumber	0.1	BNPU	-	-	-	-	-	-	3	66	7.4	5	84	6.9
			ILIS								110	6.7		103	7.4
	Spinach	0.1	BNPU	5	4	23.5	-	-	-	5	70	8.0	5	93	6.0
			ILIS								96	5.1		104	5.1
		0.1 (waiting time ca. 10 min)	BNPU							5	14	17.3			
High water + low pH	Blueberry 1	0.1	BNPU	3	61	4.9	3	63	6.6	5	82	10.3	5	79	9.4
	Blueberry 2	0.01	BNPU	-	-	-	-	-	-	5	94	3.1	-	-	-
Dry	Rice	0.1	BNPU	5	No peak	n.d.	-	-	-	-	-	-	5	85	8.9
		0.1 (waiting time ca. 10 min)	BNPU							5	17	15.0	5	39	3.6

DITHIANON

Tab. 5: Recovery data for Dithianon depending on the delay time between spiking and extraction under acidic conditions:

Extraction Method	IS	Delay between spiking native dithianon and spiking of ILIS	Delay between spiking native dithianon and extraction	Recovery rates [%]						RSD (%)
				1	2	3	4	5	Avg	
QuEChERS + 1 % FA	ILIS	No delay	No delay	118	109	103			110	6,7
	BNPU			67	70	60			66	7,4
QuEChERS + 1 % SA	ILIS	No delay	No delay	114	97	108	98	97	103	7,4
	BNPU			93	79	85	83	79	84	6,9
	ILIS	No delay	ca. 10 min	115	100	94	-	-	103	10,4
	BNPU			73	67	62	-	-	68	8,1
	ILIS	ca. 10 min	ca. 10 min (shortly after ILIS-addition)	57	57	54	-	-	56	3,5
	BNPU			51	49	50	-	-	50	2,3

DITHIANON

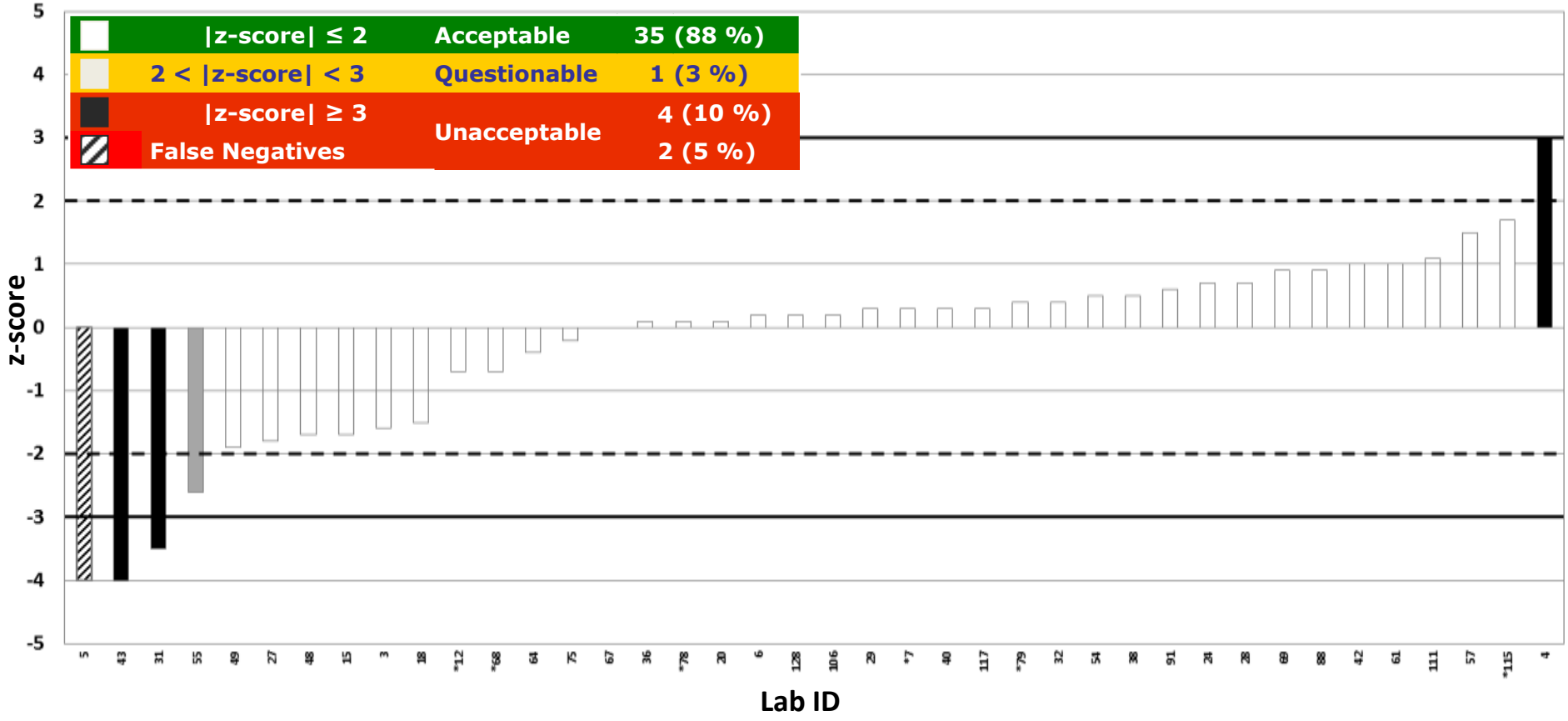
Validation data:

Tab. 3: Recovery experiments for Dithianon

Commodity	Method	n	Spiking Level [mg/kg]	Mean Recovery %	RSD %	IS
Lettuce	"QuEChERS + 1 % FA"	5	0.1	76	3.2	BNPU
	"QuEChERS + 1 % SA"	5	0.1	90	4.1	BNPU
Cucumber	"QuEChERS + 1 % FA"	5	0.1	66	7.4	BNPU
				110	6.7	ILIS
	"QuEChERS + 1 % SA"	5	0.1	84	6.9	BNPU
				103	7.4	ILIS
Spinach	"QuEChERS + 1 % FA"	5	0.1	70	8.0	BNPU
				96	5.1	ILIS
	"QuEChERS + 1 % SA"	5	0.1	93	6.0	BNPU
				104	5.1	ILIS
Blueberries	QuEChERS + 1 % FA"	5	0.1	82	10.3	BNPU
Rice	"QuEChERS + 1 % SA"	5	0.1	85	8.9	BNPU

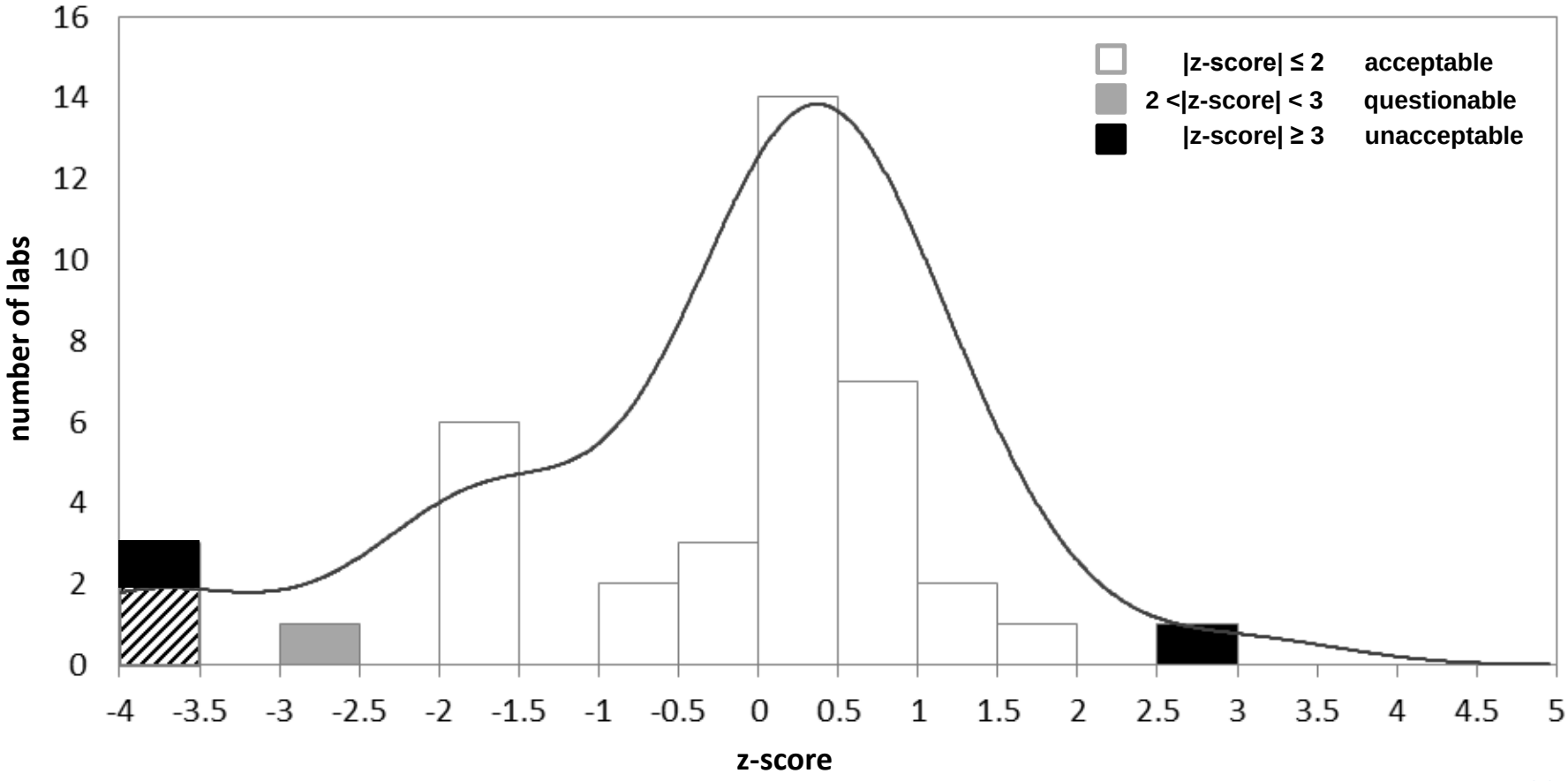
PHOSPHONIC ACID

Results	38
False Neg.	2
AV	9.831 [mg/kg]
CV*	29.5 %
MRRL	0.05 [mg/kg]



PHOSPHONIC ACID

Results	38
False Neg.	2
AV	9.831 [mg/kg]
CV*	29.5 %
MRRL	0.05 [mg/kg]



PHOSPHONIC ACID

Results	38
False Neg.	2
AV	9.831 [mg/kg]
CV*	29.5 %
MRRL	0.05 [mg/kg]

	ALL	Using ILIS	Not using ILIS
Number of Results	38	15	23
Robust Mean	9.83	10.28	9.50
CV*	30 %	30 %	29 %
Vesus AV	**0 %**	+ 5%	- 3 %
Versus Rec. Corr.	-4 %	**0 %**	- 8 %

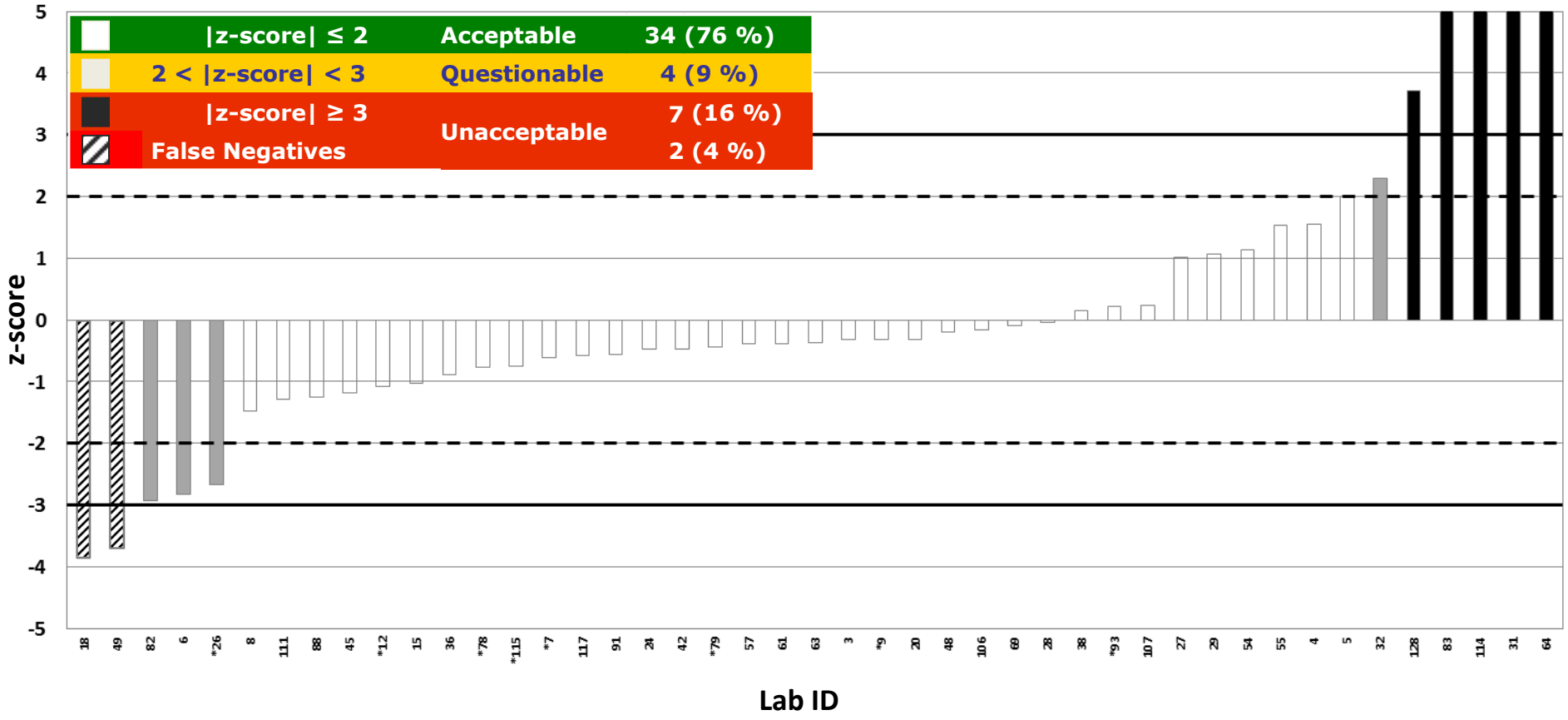
EURL-SRM

PERCHLORATE (ANION)

PERCHLORATE

FOR INFORMATIVE PURPOSE ONLY

Results	43
False Neg.	2
AV	0.260 [mg/kg]
CV*	35.9 %
MRRL	0.02 [mg/kg]



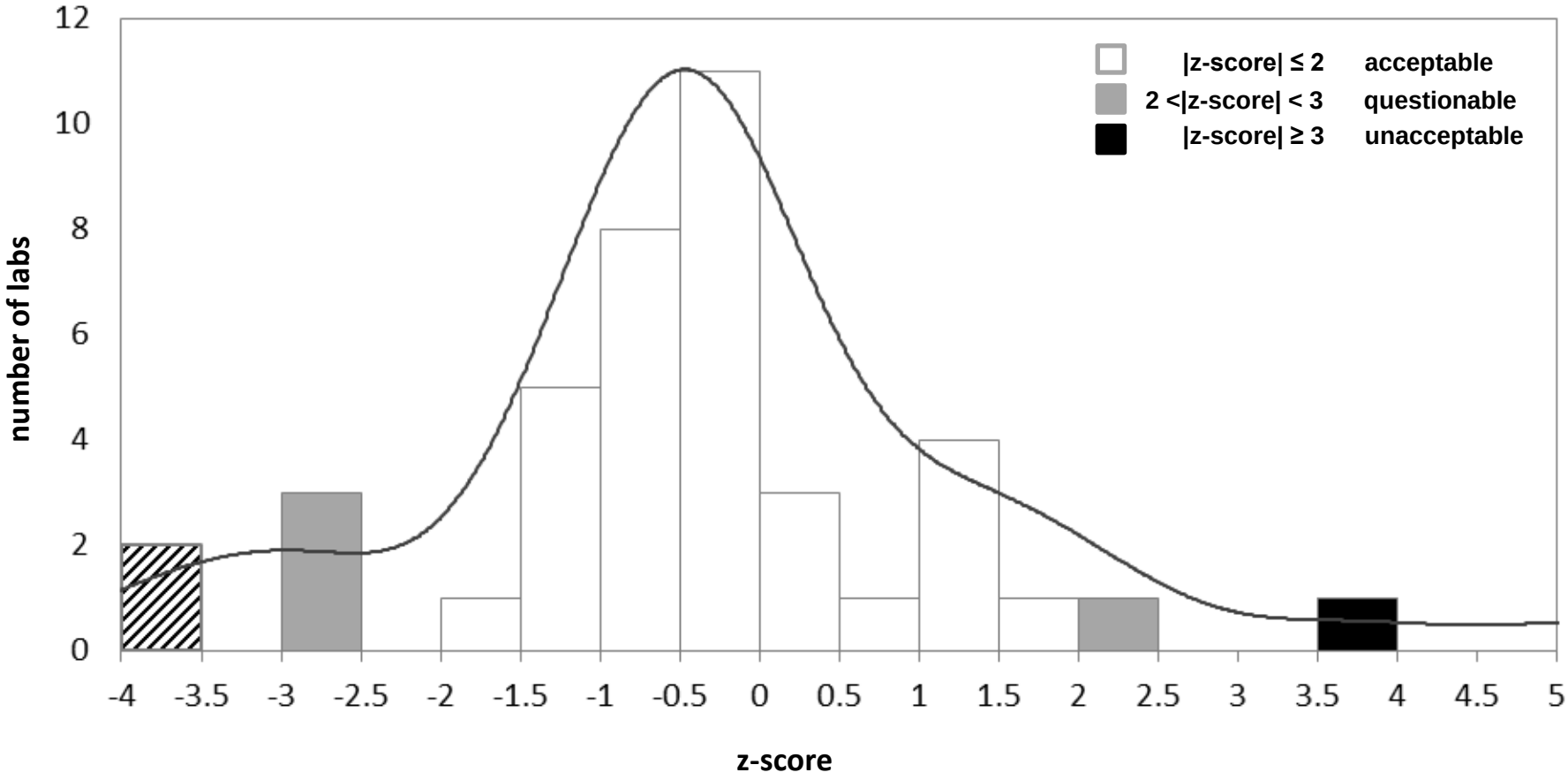
EURL-SRM

PERCHLORATE (ANION)

PERCHLORATE

FOR INFORMATIVE PURPOSE ONLY

Results	43
False Neg.	2
AV	0.260 [mg/kg]
CV*	35.9 %
MRRL	0.02 [mg/kg]



EURL-SRM

PERCHLORATE (ANION)

PERCHLORATE

FOR INFORMATIVE PURPOSE ONLY

Results	43
False Neg.	2
AV	0.260 [mg/kg]
CV*	35.9 %
MRRL	0.02 [mg/kg]

	ALL	Using ILIS	Not using ILIS
Number of Results	43	23	21
Robust Mean	0.260	0.234	0.300
CV*	36%	24%	56%
Vesus AV	**0 %**	**-** 10%	**+** 15 %
Versus Rec. Corr.	+11%	**0 %**	+28 %

Topics

EURL-SRM Network
NRL-SRM Network

Proficiency Tests
EUPT-SRM Overview
EUPT-SRM11 (Spinach)
EUPT-SRM10 (Corn)
EUPT-SRM9 (Milk)

Workshops
Workshop Overview
Joint Workshop 2015
Workshop AO/SRM 2014

Services
ILISs Distribution Service
CheckYourScope-Service
SRM-PinBoard Service
List of Methods
List of Observations

ILIS Distribution Service

The EURL for Pesticide Residues Requiring Single Residue Methods (EURL-SRM) offers stock solutions of isotopically labelled internal standards (ILISs).

ILIS solutions: currently available:

	Compound	Concentration (solvent)	Volume	Sufficient for**	Price***
1	$^{18}O_3$-Chlorate*	~200 µg/ml (H_2O)	1 ml	100 Samples	75 €
2	$^{18}O_3$-Chlorate*	~200 µg/ml (H_2O)	5 ml	500 Samples	250 €
3	$^{18}O_3$-Phosphonate	~2 mg/ml (^{18}O-H_2O)	1 ml	1000 Samples	125 €

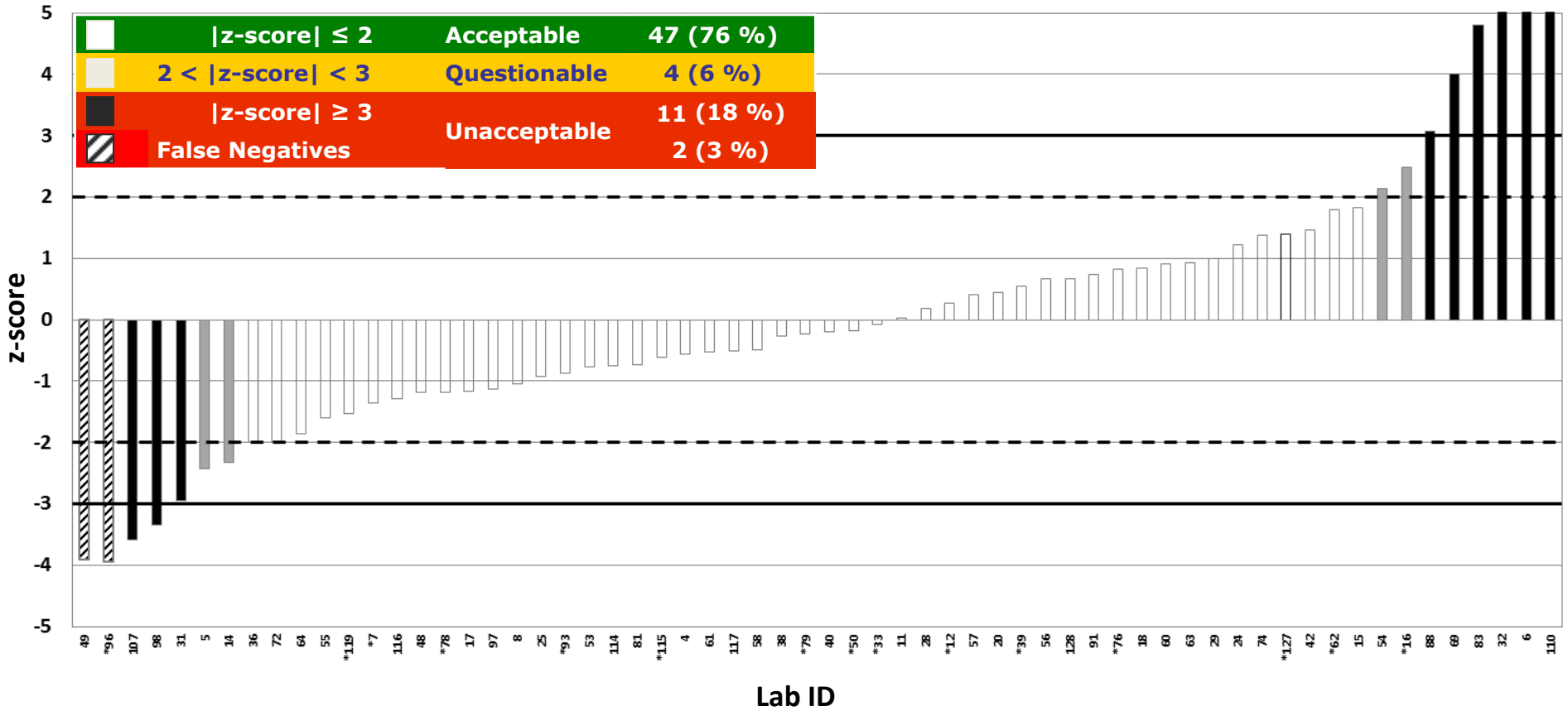
* Due to manufacturing process the stock solution of $^{18}O_3$-chlorate is accompanied by $^{18}O_4$-perchlorate (ca. 40 µg/ml).

** if added to sample portions prior to extraction

*** **final prize** including delivery fee, no VAT will be charged

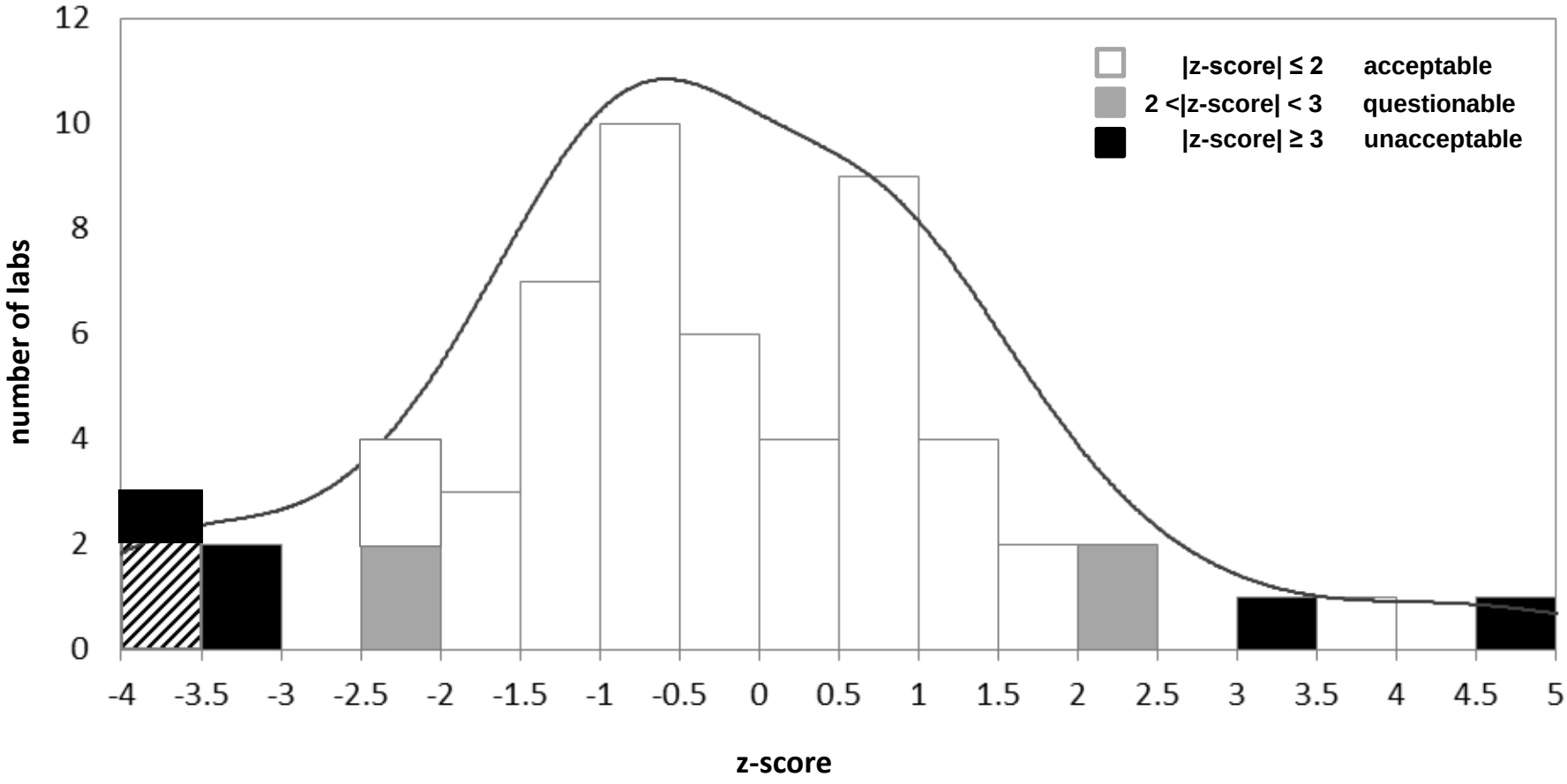
PYMETROZINE

Results	60
False Neg.	2
AV	0.432 [mg/kg]
CV*	42.3%
MRRL	0.01 [mg/kg]



PYMETROZINE

Results	60
False Neg.	2
AV	0.432 [mg/kg]
CV*	42.3%
MRRL	0.01 [mg/kg]



PYMETROZINE

Results	60
False Neg.	2
AV	0.432 [mg/kg]
CV*	42.3%
MRRL	0.01 [mg/kg]

	ALL	Recovery Correction applied	No Recovery Correction
Number of Results	60	25	32
Robust Mean	0.432	0.479	0.371
CV*	42%	32%	41%
Vesus AV	**100 %**	+ 11%	- 14 %
Versus Rec. Corr.	-10%	**100 %**	-23 %

EURL-SRM

PYMETROZINE

European Commission

EURL-SRM

EU Reference Laboratories for Residues of Pesticides

Single Residue Methods

EURL-SRM - Analytical Observations Report

concerning the following…

- **Compound(s)**: Pymetrozine
- **Commodities**: Various commodities of plant origin
- **Method(s)**: QuEChERS, adjustment of pH
- **Instrumentation**: LC-MS/MS

Analysis of Pymetrozine by the QuEChERS Method - Impact of pH on Recovery Rate

Reported by: EURL-SRM

Version 1 (last update: 18.04.2016)

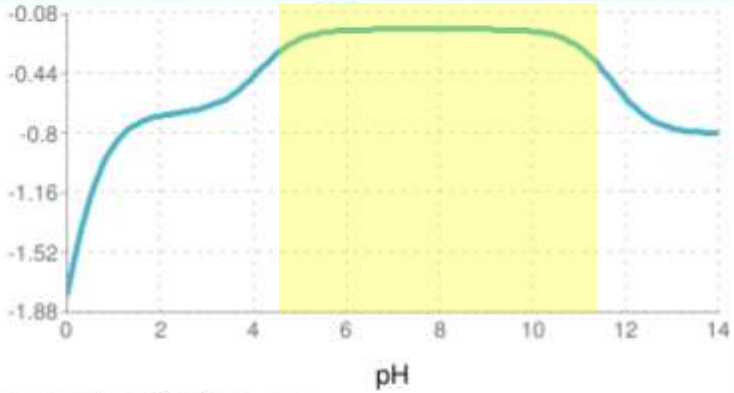
PYMETROZINE

Table 1: Recovery rates for pymetrozine using citrate buffered QuEChERS (EN15662)

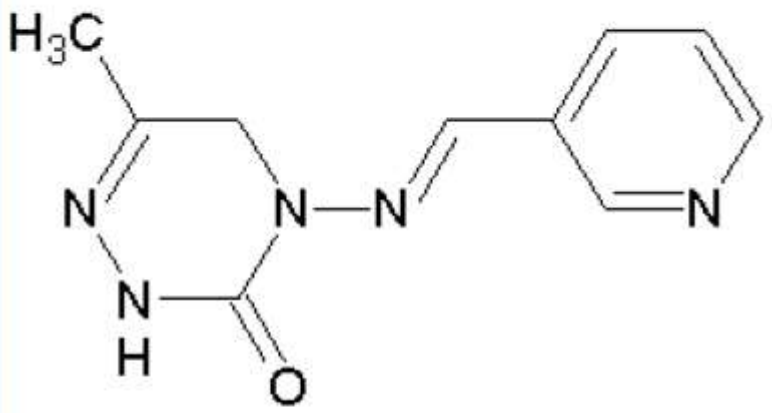
Commodity	n	Level [mg/kg]	Recovery rates by QuEChERS EN 15662, (Spiking level 0.1 mg/kg)	CV
Cucumber	5	0.01	62 %	5 %
Avocado	5	0.01	59 %	10 %
Wheat	5	0.1	58 %	6 %
Grapes	5	0.1	55 %	4 %
Lemon	4	0.1	46 %	6 %

PYMETROZINE

Facts at a glance:

Pymetrozine	
Mode of action	Insecticide selective against Homoptera like aphids and whiteflies [1]
Log D	 www.chemicalize.org
Partition coefficient	log Po/w = -0.19 (pH 5, 25 °C) log Po/w = -0.19 (pH 7, 25 °C) log Po/w = -0.20 (pH 9, 25 °C) [3]
Water solubility	320 mg/L (25 °C; pH 5) 270 mg/L (25 °C; pH 7) 270 mg/L (25 °C; pH 9), all 99.7% [3]
Dissociation constant	pKa,1 = 4.06 (basic, protonation at nitrogen atom of the pyridine ring) [1,3] pKa,2 < 1 (basic, protonation at nitrogen atom of triazinone ring) [1,3] pka,3 = 11.4 (acidic, deprotonation at nitrogen of triazinone ring) [chemicalize.org]

Pymetrozine



PYMETROZINE

Table 3: pH values of QuEChERS extracts using different buffering salt combinations

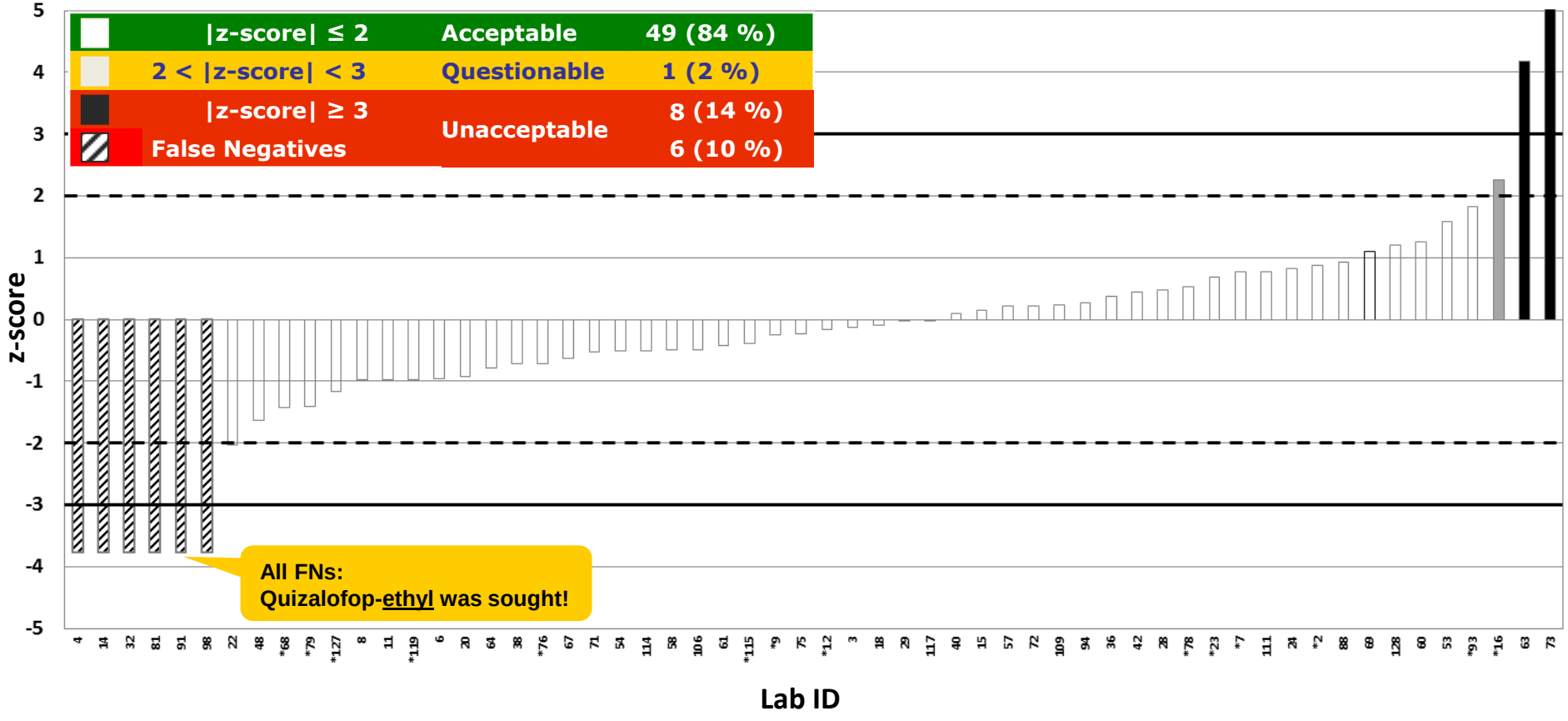
Salt mixture	pH-values of QuEChERS extracts (measured at ~ 23 °C)		Recovery rates of Pymetrozine (n=2) at 0.1 mg/kg	
	Orange juice	Cucumber	Orange juice	Cucumber
Citrate buffering salts EN15662	3.88	4.20	55 %	65 %
4 g $MgSO_4$. 1 g NaCl	2.55	4.84	22 %	80 %
4 g $MgSO_4$. 1 g NaCl. 0.5 g Na-Acetate	5.21	6.55	94 %	86 %
4 g $MgSO_4$. 0.5 g Mg-Acetate	5.33	6.63	Not analyzed	Not analyzed
4 g $MgSO_4$. 1 g Mg-Acetate	5.54	6.63	89 %	97 %

EURL-SRM

QUIZALOFOP (FREE ACID*)

QUIZALOFOP

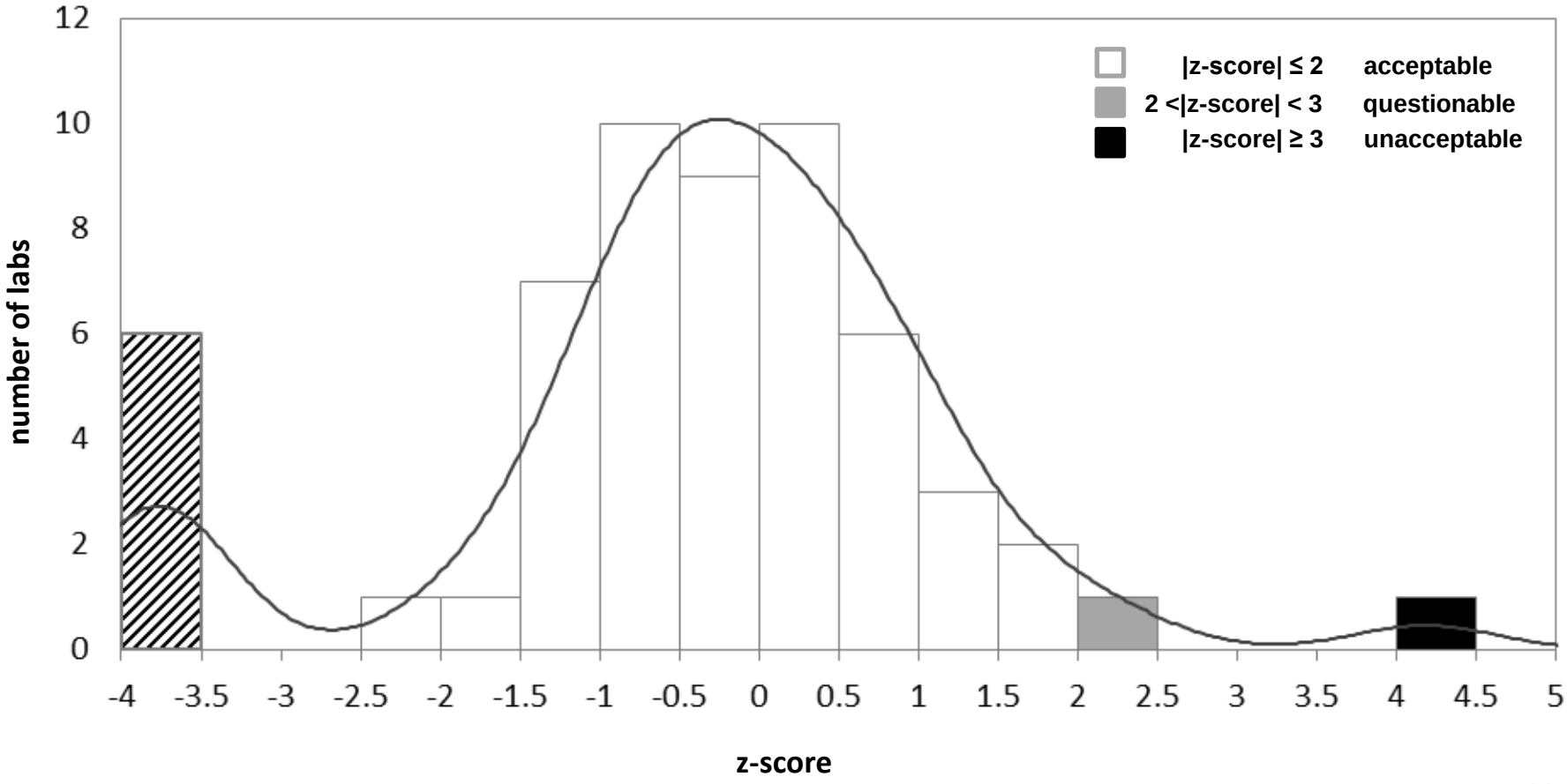
Results	52
False Neg.	6
AV	0.171 [mg/kg]
CV*	24.6 %
MRRL	0.01 [mg/kg]



QUIZALOFOP (FREE ACID*)

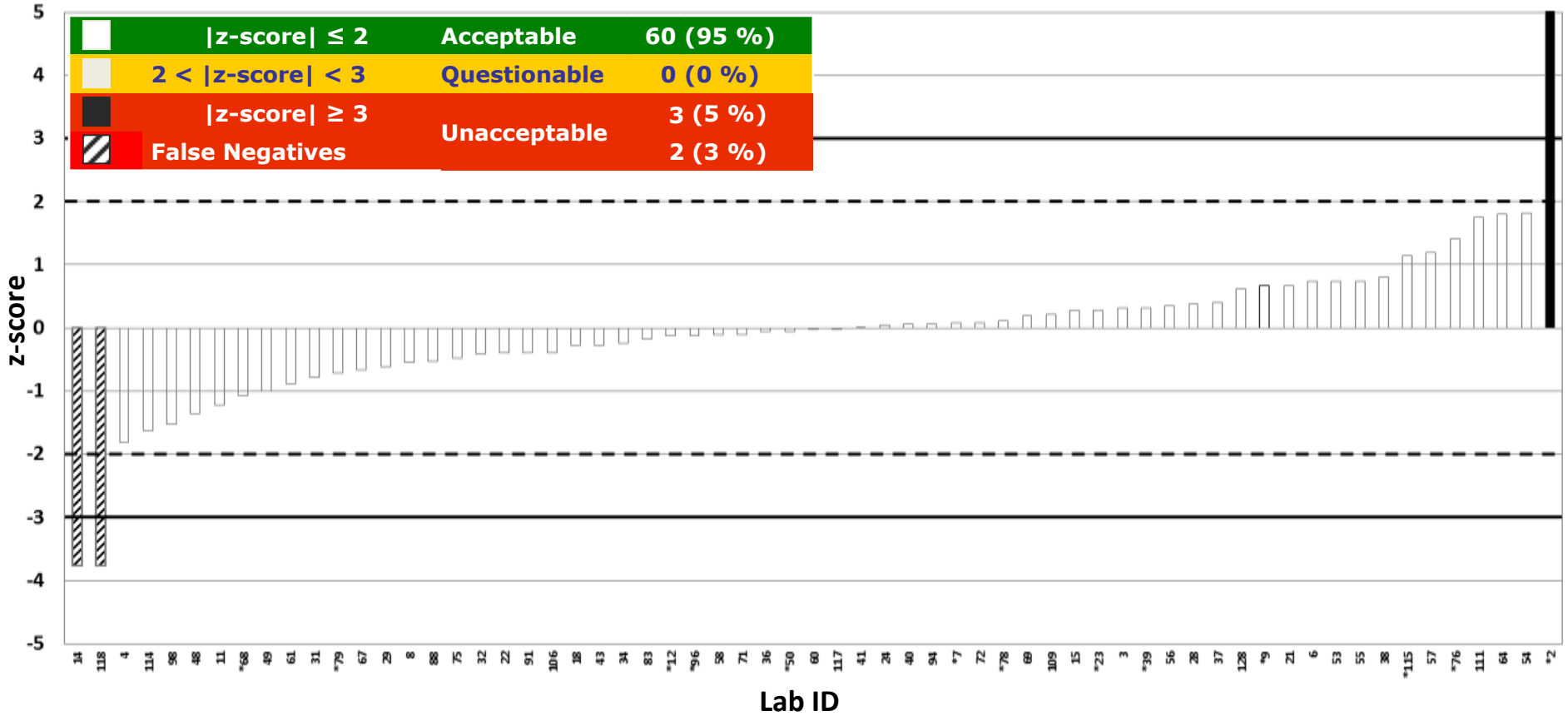
QUIZALOFOP

Results	52
False Neg.	6
AV	0.171 [mg/kg]
CV*	24.6 %
MRRL	0.01 [mg/kg]



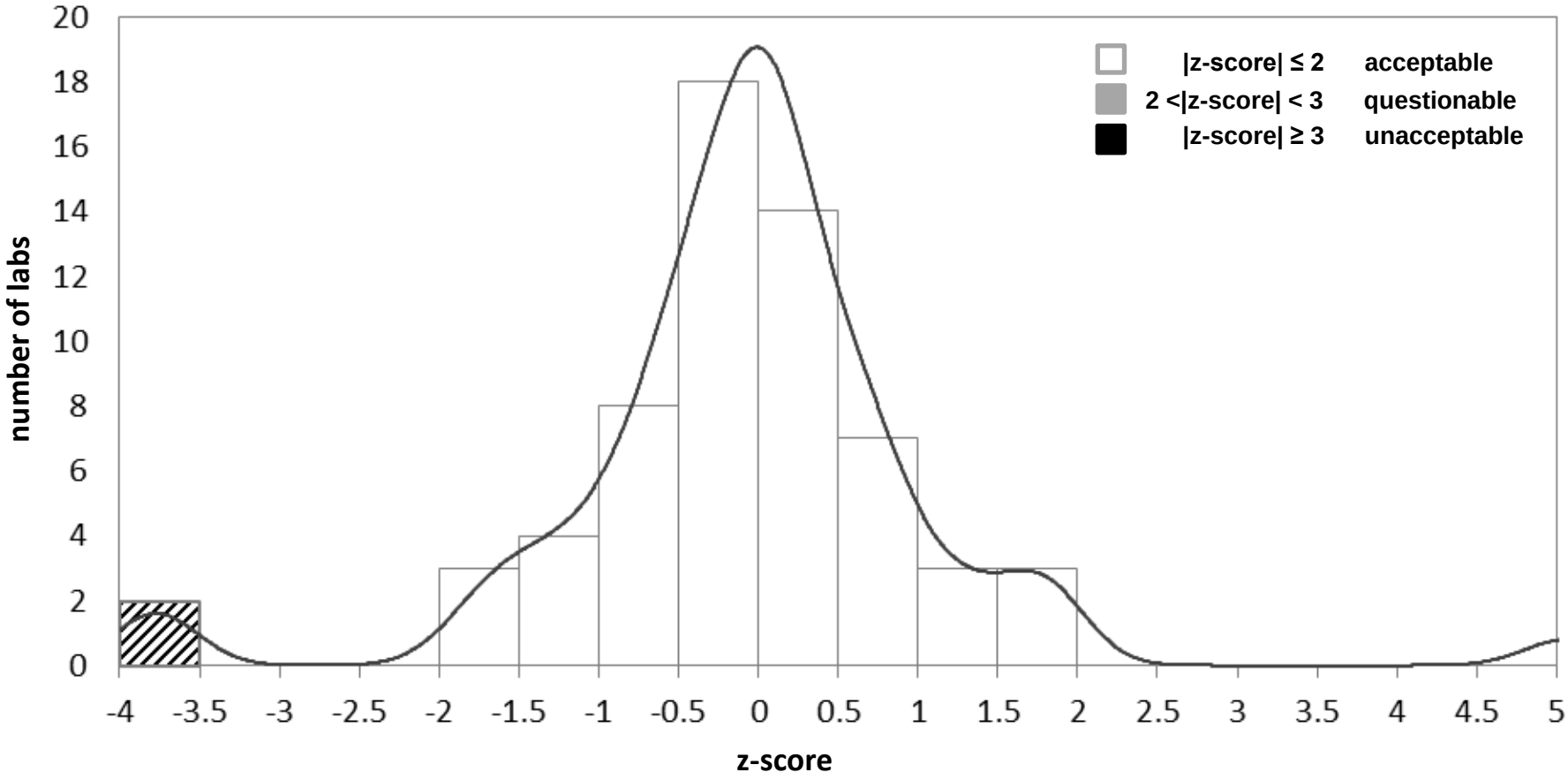
TRICLOPYR

Results	61
False Neg.	2
AV	0.177 [mg/kg]
CV*	18.7 %
MRRL	0.01 [mg/kg]



TRICLOPYR

Results	61
False Neg.	2
AV	0.177 [mg/kg]
CV*	18.7 %
MRRL	0.01 [mg/kg]



BENEFIT OF USING ILISs

Impact of ILIS on CV*s

[1] labs reporting info about ILIS use
[2] among labs reporting info about ILIS use
[3] Avg of AAZ-values in this table (not calculated from z-scores)

Compound	ALL			WITH ILIS			W/O ILIS		
	No. of Labs	CV*	AAZ	%[2]	CV*	AAZ	%[2]	CV*	AAZ
COMPULSORY									
Cyromazine	88/82[1]	31.8%	1.1	15%	19.8%	0.7	86%	34.0%	1.2
OPTIONAL									
Chlorate	46/41[1]	44.6%	1.6	54%	15.6%	0.6	46%	68.4%	2.1
Phosphonate	40/35[1]	29.5%	1.0	43%	30.3%	0.9	57%	33.0%	1.1
Perchlorate	45/42[1]	35.9%	1.9	55%	23.5%	0.9	45%	54.6%	1.8
AVERAGE		35%	1.4[3]		22%	0.8[3]		58%	1.7[3]

Avg. deviation from AV =19%

= 39%

EURL-SRM

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
Cyromazine	86	31.8	1.512	+/- 0.0648	0.1134	passed
DTCs	94	34.6	1.297	+/- 0.0579	0.0973	passed
Dodine	83	26.2	1.243	+/- 0.0447	0.0932	passed
TFNA	62	20.0	0.756	+/- 0.0240	0.0567	passed
TFNG	63	20.7	0.448	+/- 0.0146	0.0336	passed
Tolylfluanid	83	57.4	*0.598*	+/- 0.0471	0.0448	failed

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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
BAC-C14	58	25.8	0.285	0.0121	0.0213	passed
Chlorate	43	44.6	2.033	0.1730	0.1525	passed
Dithianon	36	94.3	*1.729*	0.3397	0.1297	failed
Phosphonic acid	38	29.5	9,831	0.5884	0.7373	passed
Perchlorate	43	35.9	0.260	0.0178	0.0195	passed
Pymetrozine	60	42.3	*0.432*	0.0295	0.0324	passed
Quizalofop	52	24.6	0.171	0.0073	0.0128	passed
Triclopyr	61	18.7	0.177	0.0053	0.0133	passed

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OVERALL PERFORMANCE I: COMPULSORY COMPOUNDS

Compulsory compounds:

EU+EFTA

Compound	No. of Labs	FNs	AAZ	CV* [%]	☺ A	😐 Q	☹ U
Cyromazine	88	2	1.1	31.8	83 %	10 %	7 %
Dithiocarbamates	95	1	1.2	34.6	82 %	6 %	12 %
Dodine	83	0	1.0	26.2	88 %	4 %	8 %
TFNA	63	1	0.8	20.0	94 %	0 %	6 %
TFNG	63	0	0.7	20.7	92 %	5 %	2 %
Tolylfluanid	87	4	1.9	57.4	62 %	13 %	25 %

Optional Compounds:

EU+EFTA

Compound	No. of Labs	FNs	AAZ	CV* [%]	☺ A	😐 Q	☹ U
BAC-C14	58	0	0.9	25.8	95 %	0 %	5 %
Chlorate	46	3	1.6	44.6	72 %	13 %	15 %
Dithianon	39	3	3.0	94.3	28 %	15 %	56 %
Phosphonic acid	40	1	1.1	29.5	88 %	3 %	10 %
Perchlorate	45	2	1.5	35.9	76 %	9 %	16 %
Pymetrozine	62	2	1.6	42.3	76 %	6 %	18 %
Quizalofop	58	6	1.2	24.6	84 %	2 %	14 %
Triclopyr	63	2	0.8	18.7	94 %	0 %	5 %

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OVERALL PERFORMANCE III

Rules for Category A:

EU+EFTA

- Analysed for at least 9 out of 11 compulsory pesticides
- Correct found for at least 5 out of 6 compulsory pesticides present in test item
- No FPs

	No. of Labs	[%]
Category A	56	45 %
Category B	68	55 %

Using the old rule : Cat A: 63 (51%); **Cat** B: 61 (49%)

METHODS EMPLOYED BY EUPT PARTICIPANTS

EUPT-SRM 11 (2016) Methods employed	QuEChERS* (diff. versions)	QuPPe	SweEt	Mini-Luke + C19	Liq-Liq P./ Spectroph./ Head Space
BAC-C14	88%			2%	
Chlorate		87%			
Cyromazine	48%	34%	6%	1%	
Dithianon	78%		3%	3%	
Dithiocarbamates					43%/22%/22%
Dodine	82%		4%	4%	
Perchlorate		87%			
Phosphonic acid		90%			
Pymetrozine	74%		5%	5%	
Quizalofop	74%		3%	3%	
TFNA	86%		4%	2%	
TFNG	84%		4%	2%	
Tolylfluanid	67%		8%	1%	
Triclopyr	68%		5%	3%	

Reasons for Poor Performance

74 labs reported in 172 cases questionable or poor results (FN, FP, $|z|>2$)

33 labs reported in 67 cases (tentative) error sources.

Most common explanations:

- **Wrong analyte (Quizalofop-ethyl instead of quizalofop acid)**
- **Incorrect concentration of calibration solutions**
- **Human errors (transcription, calculation)**
- **Inproper or unsuitable procedure/method employed**

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Overall Evaluation

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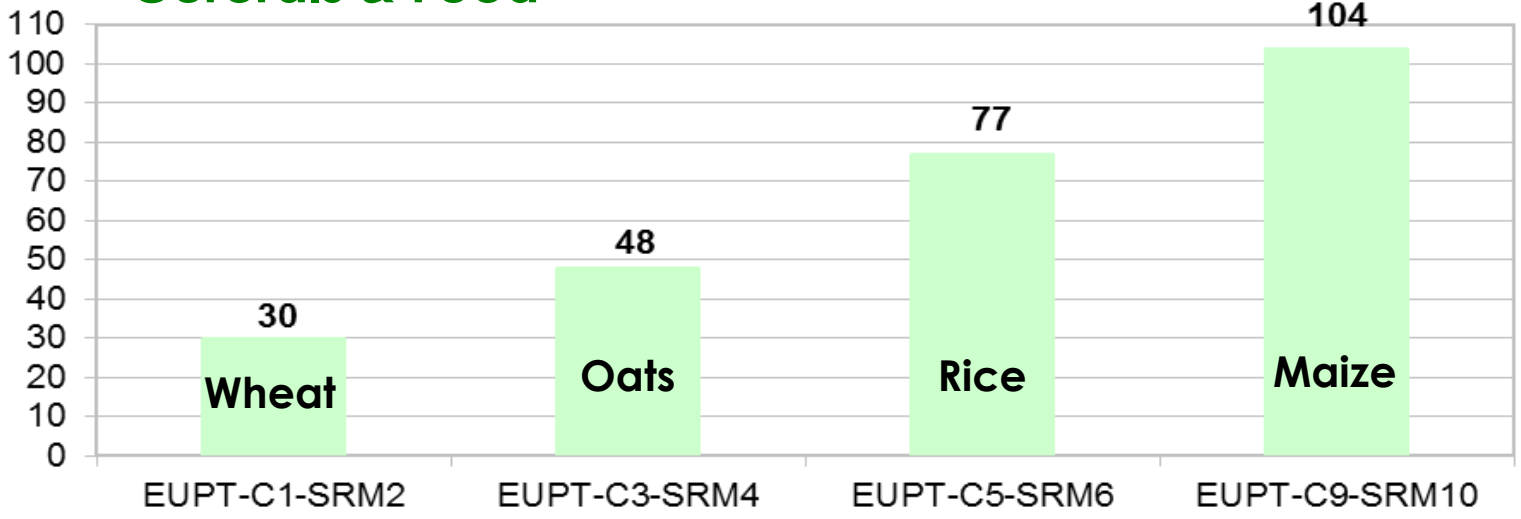
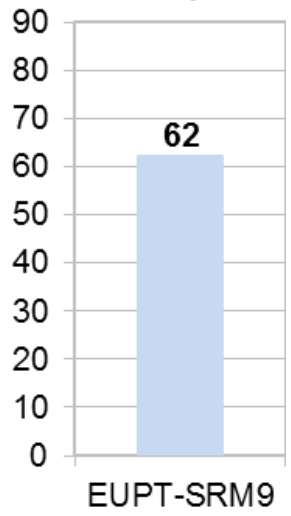
NO. OF LABS SUBMITTING RESULTS IN EUPT-SRMs

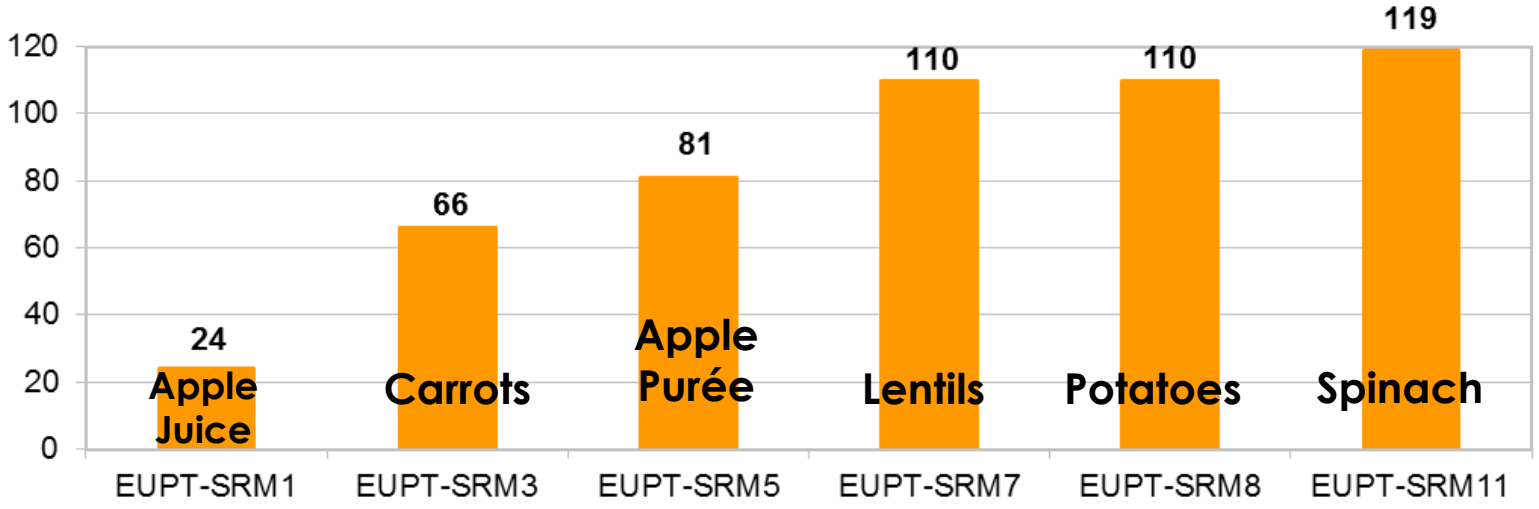
Cererals & Feed



AO



Fruits & Vegetables



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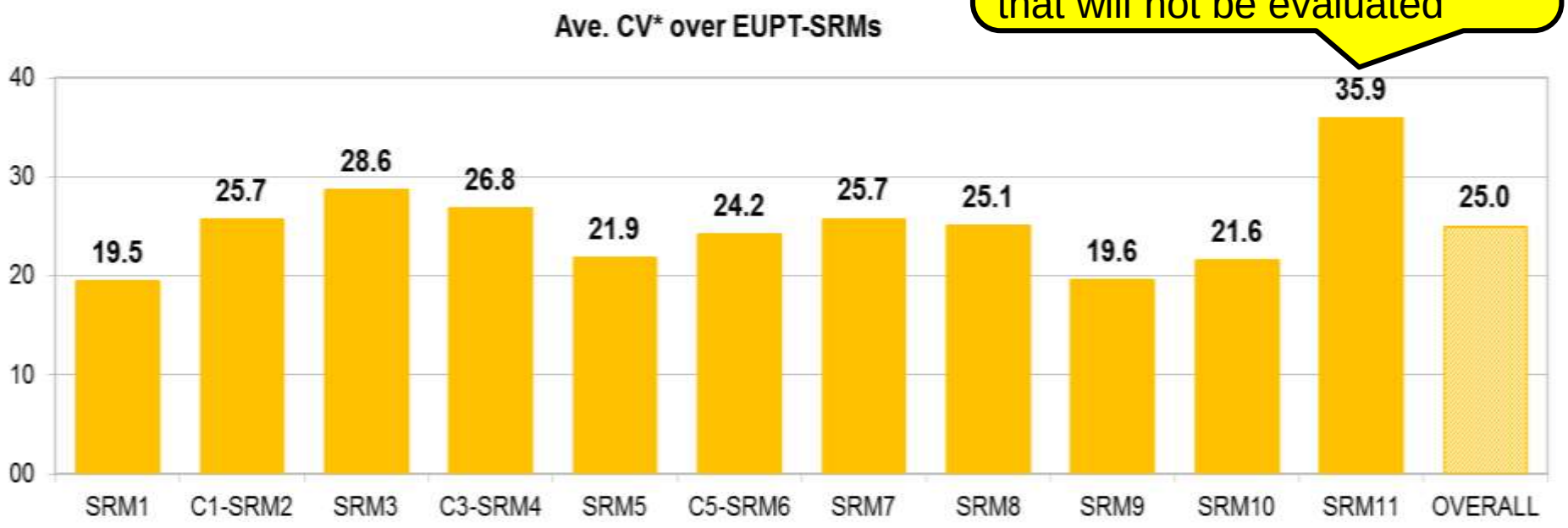
AVERAGE DATA DIESTRIBUTION EUPT-SRMs 1-11

Unlike in other PTs this figure includes Qn of compounds that will not be evaluated



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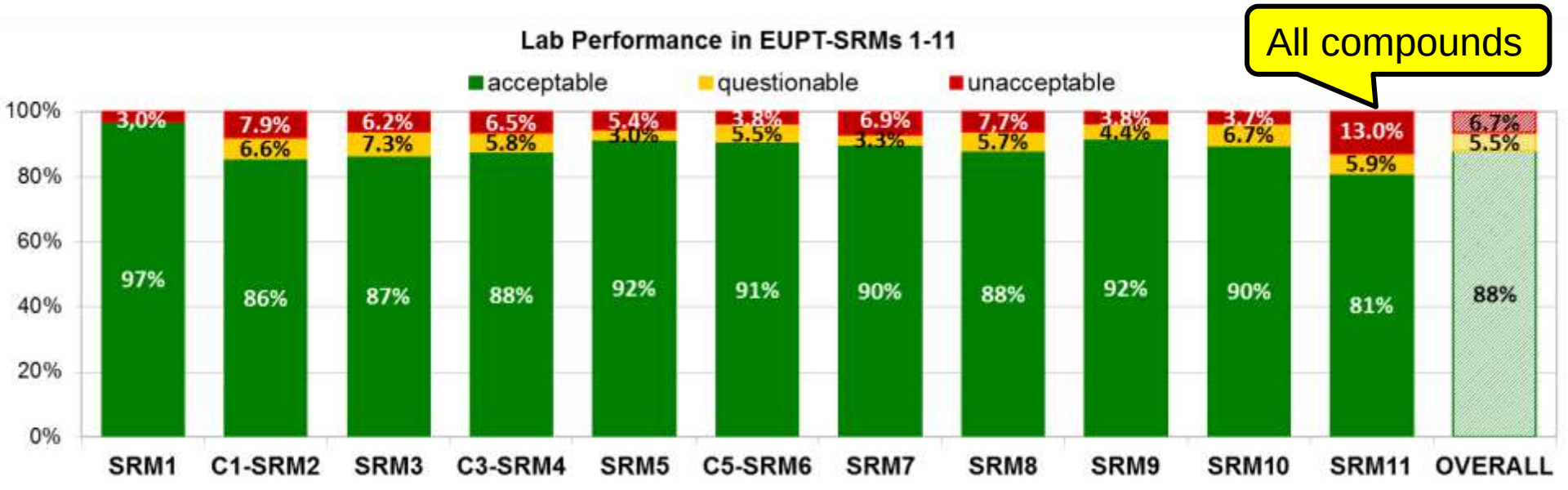
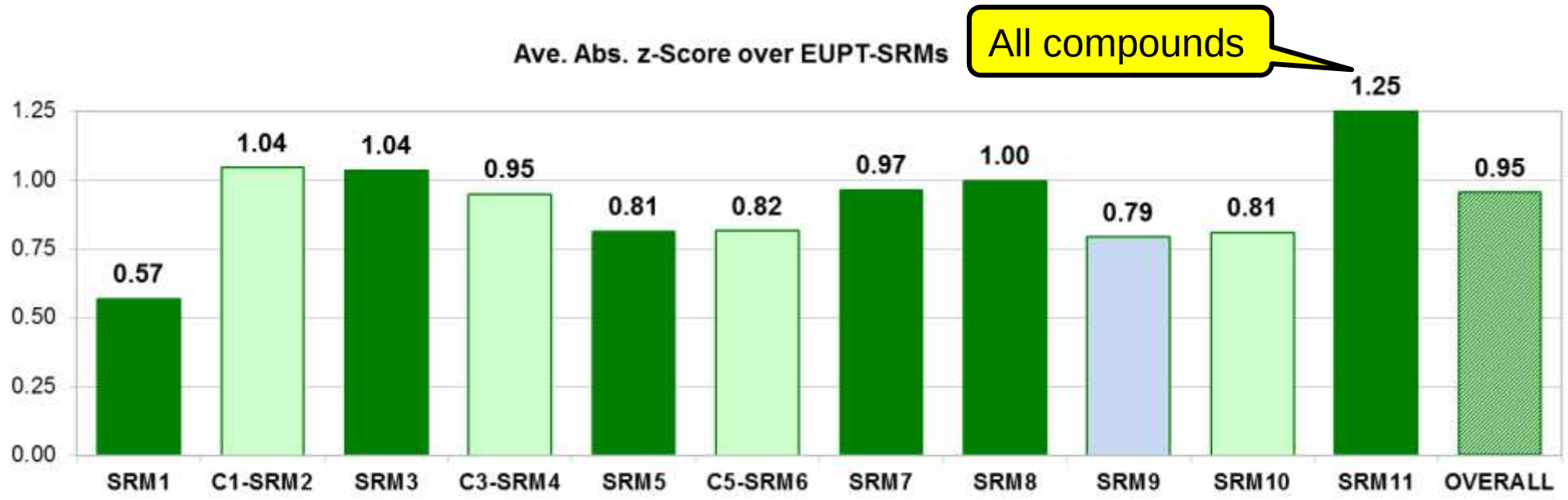
LAB PERFORMANCE IN EUPT-SRMs 1-11





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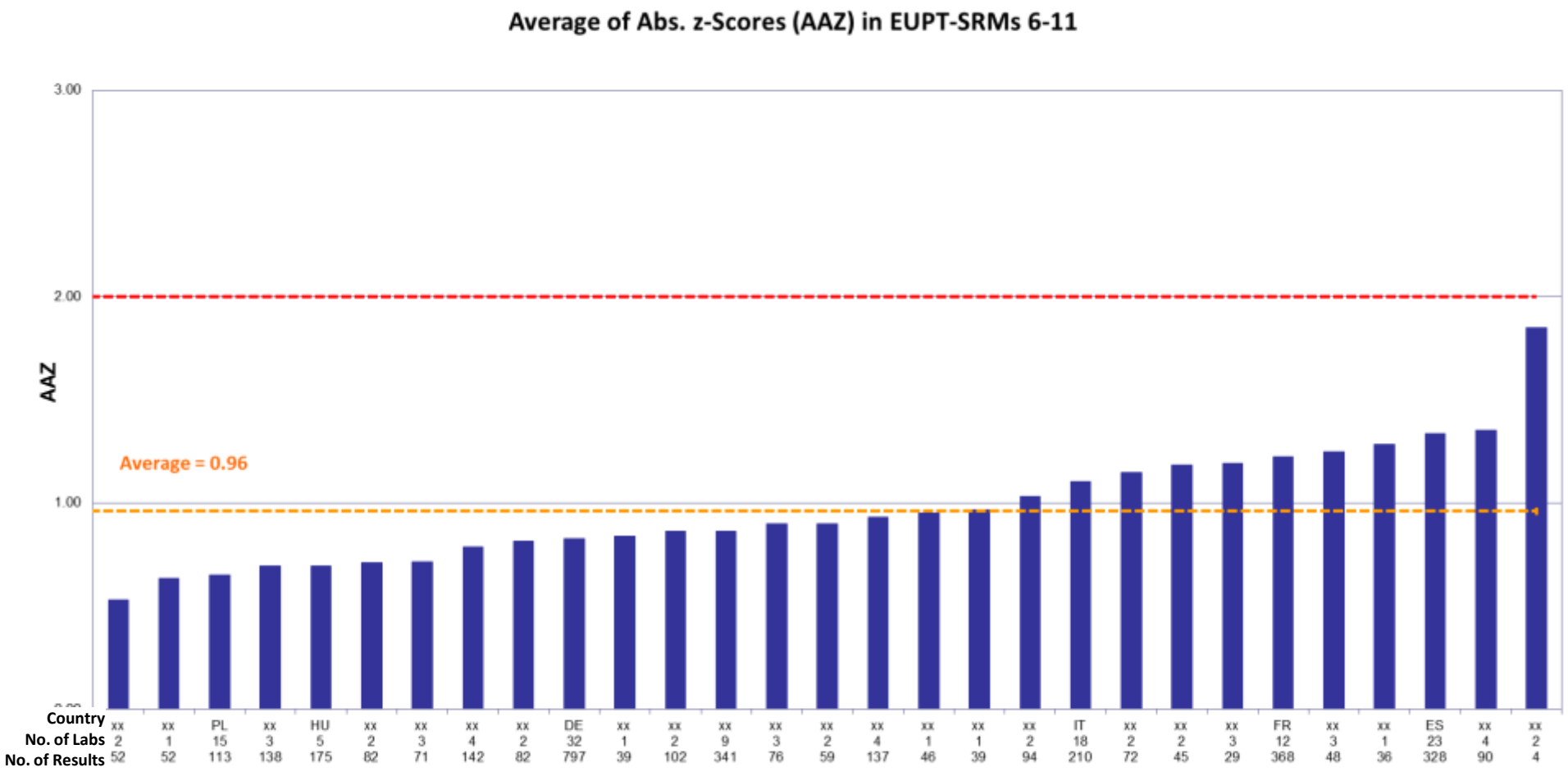
AAZ in EUPT-SRMs 6-11 (EU+EFTA)



Analytes evaluated for information only were excluded from the AAZ-calculation but considered in the No. of results.
Countries with 4 or less labs participating in the EUPT-SRM 1-11 are hidden

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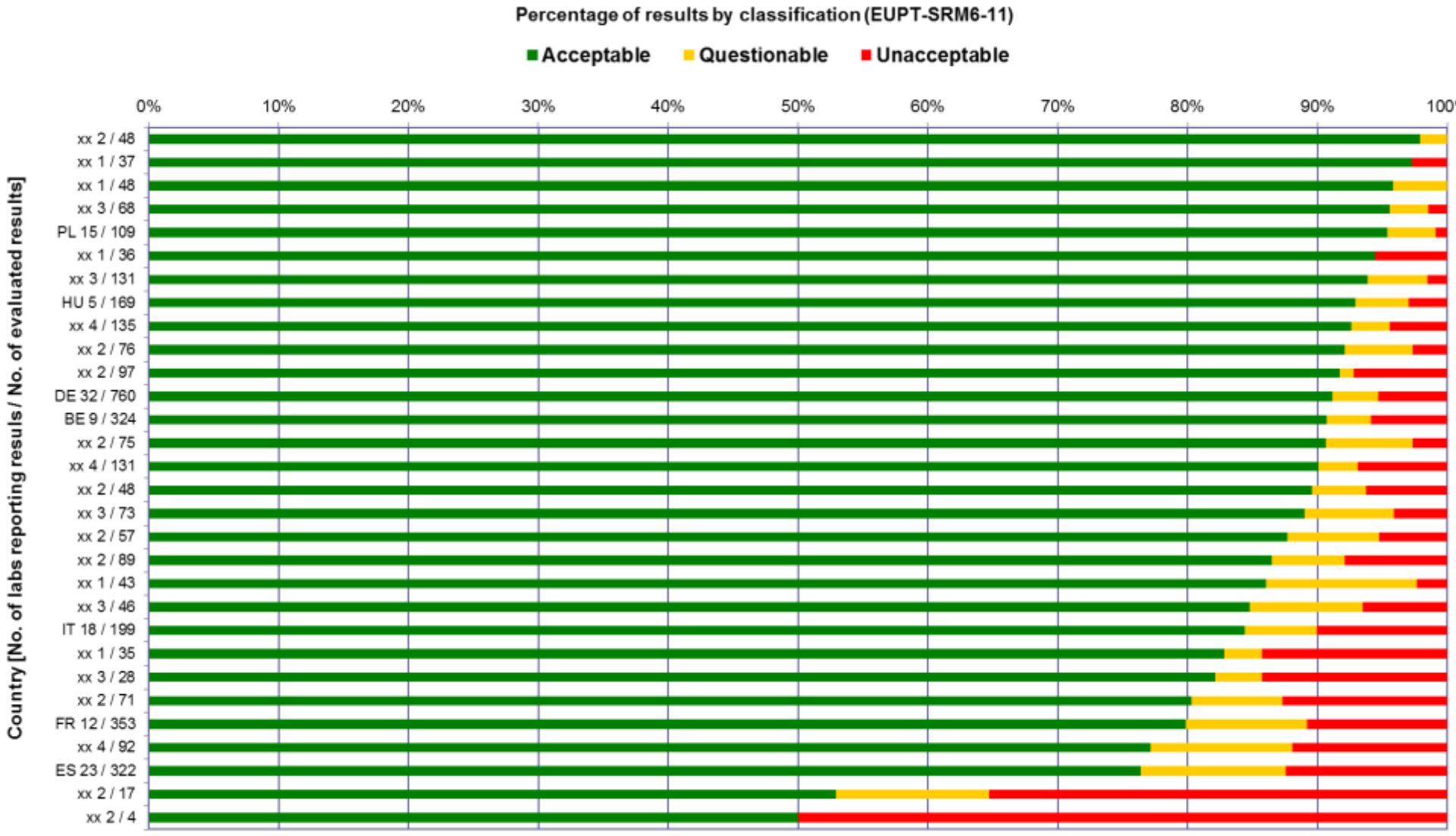
PERFORMANCE BY COUNTRY (EUPT-SRM 6-11)



Analytes evaluated for information only were excluded.

Countries with less than 4 labs participating in the EUPT-SRM 6-11 are hidden.

Thank You
for Your Attention

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