EUPT-SRM18
Pesticide Residues in Honey

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Selection of Commodity & Pesticides to be spiked

COMMODITY & DATE Selection

Decided in AdvG-Meeting in June 2022:

Commodity: HONEY (→ Later decided to use different material for SRM18 and AO18)

Timing: LAST in EUPT-season (shipment in May)

EUPT-SRM18 Organisation

Registration for EUPT-SRM18:

17 March – 6 April, 2023

Sample Shipment:

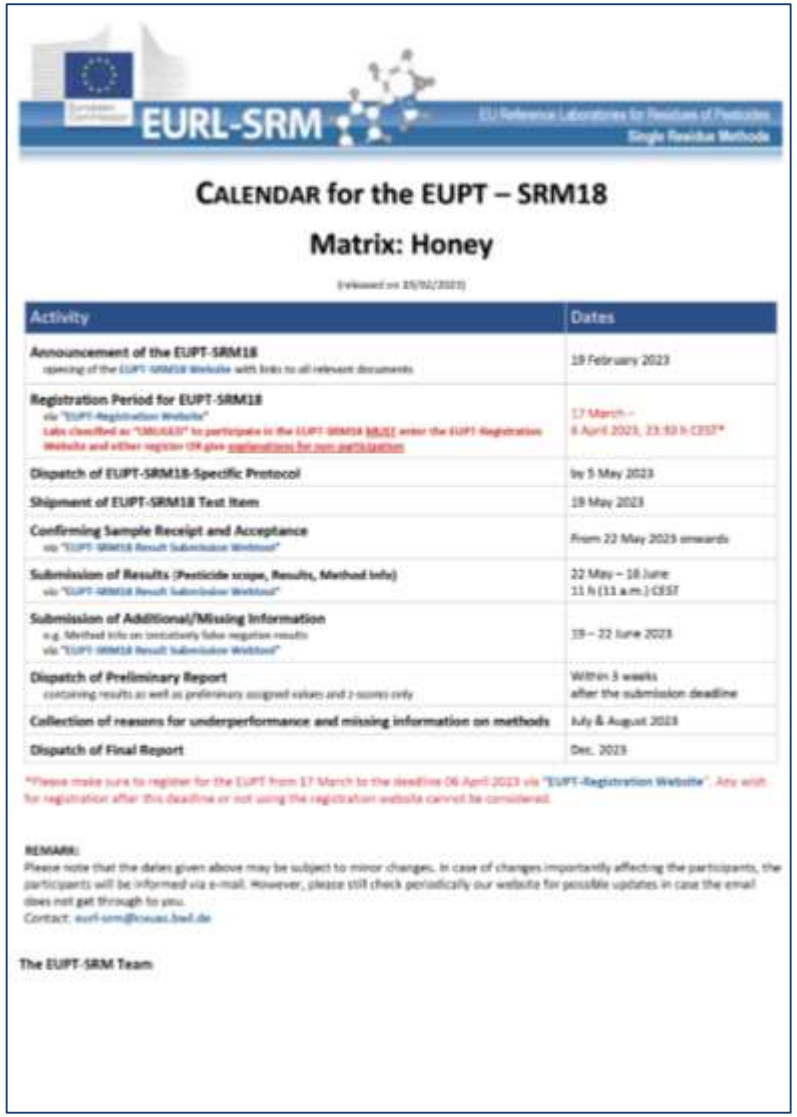
19 May, 2023

Results Submission Period:

22* May – 16 June, 2023 (*Webtool Opening)

Preliminary Report:

to be released by 14 July, 2023



EURL-SRM

EU Reference Laboratories for Residues of Pesticides
Single Residue Methods

CALENDAR for the EUPT – SRM18

Matrix: Honey

(released on 15/02/2023)

Activity	Dates
Announcement of the EUPT-SRM18 opening of the EUPT-SRM18 Website with links to all relevant documents	19 February 2023
Registration Period for EUPT-SRM18 via "EUPT-Registration Website" Labs classified as "SMU/AAD" to participate in the EUPT-SRM18 MUST enter the EUPT-Registration Website and either register OR give explanations for non-participation	17 March – 6 April 2023, 23:59 h CEST*
Dispatch of EUPT-SRM18-Specific Protocol	by 5 May 2023
Shipment of EUPT-SRM18 Test Item	19 May 2023
Confirming Sample Receipt and Acceptance via "EUPT-SRM18 Result Submission Webtool"	From 22 May 2023 onwards
Submission of Results (Pesticide scope, Results, Method Info) via "EUPT-SRM18 Result Submission Webtool"	22 May – 16 June 11 h (11 a.m.) CEST
Submission of Additional/Missing Information e.g. Method info on tentatively false negative results via "EUPT-SRM18 Result Submission Webtool"	19 – 22 June 2023
Dispatch of Preliminary Report containing results as well as preliminary assigned values and z-scores only	Within 3 weeks after the submission deadline
Collection of reasons for underperformance and missing information on methods	July & August 2023
Dispatch of Final Report	Dec. 2023

*Please make sure to register for the EUPT from 17 March to the deadline 06 April 2023 via "EUPT-Registration Website". Any wish for registration after this deadline or not using the registration website cannot be considered.

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

The EUPT-SRM Team

Selection of Commodity & Pesticides to be spiked

ANALYTE Selection - Factors considered for INCLUSION IN TARGET LIST…

a) Listing in EU monitoring documents:

- MACP-Regulation:
  - ***Mandatory:*** Chlormequat, Mepiquat, Nicotine *(MACP 2024 ff)*, Fosetyl, Phosphonic acid, Haloxyfop, Fluazifop, 2,4-D, Glyphosate
  - ***Extra****: Bromide (MRL too low for many labs), Copper (No MRL, also wish of COM)*
- Monitoring Working Document :
  - ***Mandatory*** *(from Honey List in WD) :* BAC, DDAC, Chlorate, Matrine, Oxymatrine, Amitraz (dilemma: parent, metab., full RD?), Fluazifop, Glyphosate, 2,4-D,
    Optional *(from Honey List in WD):* Chloridazon desphenyl
  - ***Optional*** *(other entries):* AMPA, NAGly, MCPA, Quizalofop, Trinexapac

b) COM-wish: Copper

c) Relevance to matrix (HONEY) – Intermediate Results of own Pilot Monitoring

d) Suggestions/Voting by EUPT-Scientific Committee

e) Capacities and Capability of Participants (and EURL): Keep no. of methods moderate: Amitraz after hydrolysis not analyzed by many labs (previous survey)

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TARGET PESTICIDES List:

for the EUPT–SRM18 (2023), Honey
(updated on 08.05.2023)

Analytes are sorted alphabetically in the same order as in the Webtool.
For grouping into Mandatory and Optional (incl. Extra): See sheet "Grouped into Mandatory-Optional"

a new category "Extra (E) is introduced:
Extra analyte, not for lab evaluation (07.05.2023)

Only mandatory (=compulsory) analytes will be considered in the scope-based classification, optional (=voluntary) and extra analytes not.
Please also refer to the EUPT General Protocol.

M: Mandatory O: Optional E: Extra	Analytes	Notes	Listed in	MRRL [mg/kg]	
M	2,4-D (free acid)	No hydrolysis required	WD-Honey and MACP-Reg.	0.01	
O	AMPA		WD-Annex II (future RD)	0.01	
M	BAC-C12 chloride	Benzyldimethyldodecylammonium-chloride	WD-Honey	0.01	
M	BAC-C14 chloride	Benzyldimethyltetradecylammonium-chloride	WD-Honey	0.01	
E	Bromide (anion)	Analysis of natural content for information only (no z-score calculations)	MACP-Reg.	none	Changed to category "Extra" (07.05.2023)
M	Chlorate (anion)		WD-Honey	0.01	
O	Chloridazon desphenyl		WD-Honey	0.02	New! (05.04.2023)
M	Chlormequat chloride	Expressed as chloride salt!	MACP-Reg.	0.01	
E	Copper	Analysis of natural content for information only (no z-score calculations)	MACP-Reg.	none	New on the TPL in the category "Extra"! (08.05.2023)
M	DDAC-C10 chloride	Didecyldimethylammonium-chloride	WD-Honey	0.01	
~~M~~	~~DMF~~	~~N-(2,4-Dimethyl-phenyl)-formamide (Amitraz-metabolite)~~	~~WD-Honey~~	~~0.01~~	removed from the TPL (05.04.2023)
~~M~~	~~DMPF~~	~~N-2,4-Dimethylphenyl-N'-methylformamidine (Amitraz-metabolite)~~	~~WD-Honey~~	~~0.01~~	removed from the TPL (05.04.2023)
M	Fluazifop (free acid, sum of isomers)	No hydrolysis required	WD-Honey and MACP-Reg.	0.01	
M	Fosetyl		MACP-Reg.	0.01	
M	Glyphosate		WD-Honey and MACP-Reg.	0.01	
M	Haloxyfop (free acid, sum of isomers)	No hydrolysis required	MACP-Reg.	0.01	
M	Matrine		WD-Honey	0.01	
O	MCPA (free acid)	No hydrolysis required	WD-Annex III	0.01	
M	Mepiquat chloride	Expressed as chloride salt!	MACP-Reg.	0.01	
O	N-Acetyl-glyphosate		WD-Annex II (future RD)	0.01	
M	Nicotine		MACP-Reg. (2024 onwards)	0.01	
M	Oxymatrine		WD-Honey	0.01	
O	Perchlorate		Contaminant	0.01	
M	Phosphonic acid		MACP-Reg.	0.02	
O	Quizalofop (free acid, sum of isomers)	No hydrolysis required	WD-Annex III	0.01	
O	Trinexapac (free acid)	No hydrolysis required	WD (4.1 and Annex II)	0.01	

EURL-SRM

PESTICIDES INCURRED AND SPIKED

OVERVIEW:
COMPOUNDS APPLIED IN LAB AND INCURRED ONES

		residues incurred	compounds spiked in the lab	Compound form used for spiking in the lab
2,4-D (free acid)	COMPULSORY	-	✓	2,4-D (free acid)
BAC-C14 Chloride	COMPULSORY	-	✓	BAC-C14 Chloride
Chlorate (anion)	COMPULSORY	-	✓	Sodium-Chlorate
DDAC-C10 chloride	COMPULSORY	-	✓	DDAC-C10 chloride
Fluazifop (free acid)	COMPULSORY	-	✓	Fluazifop (free acid)
Glyphosate	COMPULSORY	-	✓	Glyphosate
Matrine	COMPULSORY	-	✓	Matrine
Nicotine	COMPULSORY	-	✓	Nicotine
Oxymatrine	COMPULSORY	-	✓	Oxymatrine
Phosphonic acid	COMPULSORY	-	✓	Phosphonic acid
Perchlorate (anion)	OPTIONAL	-	✓	Sodium-Perchlorate
Trinexapac (free acid)	OPTIONAL	-	✓	Trinexapac (free acid)
Bromide (anion)	OPTIONAL	traces	-	-
Copper	OPTIONAL	traces	-	-

Preparation of PT-Item

25 kg honey

Filling into Container and Spiking

Homogenization with Rapido ® stirrer

Bottling into Special Bucket with Tap

Preparation for Shipment

Express-Shipment to Participants

Homogeneity TEST

COMPULSORY Compounds

	2,4-D	BAC-C14	Chlorate	DDAC-C10	Fluazifop
Sample	Concentration [mg/kg]				
No. 001	0.0523 / 0.0532	0.104 / 0.106	0.109 / 0.108	0.143 / 0.144	0.0627 / 0.0617
No. 004	0.0525 / 0.0542	0.105 / 0.106	0.106 / 0.108	0.144 / 0.145	0.0636 / 0.0635
No. 020	0.0541 / 0.0538	0.108 / 0.106	0.107 / 0.109	0.149 / 0.149	0.0631 / 0.0630
No. 048	0.0535 / 0.0539	0.108 / 0.106	0.107 / 0.110	0.142 / 0.145	0.0618 / 0.0637
No. 067	0.0530 / 0.0527	0.103 / 0.103	0.109 / 0.107	0.139 / 0.145	0.0625 / 0.0620
No. 074	0.0531 / 0.0534	0.106 / 0.104	0.106 / 0.108	0.150 / 0.145	0.0640 / 0.0614
No. 89	0.0536 / 0.0526	0.106 / 0.106	0.107 / 0.109	0.145 / 0.143	0.0635 / 0.0610
No. 099	0.0539 / 0.0539	0.105 / 0.103	0.108 / 0.109	0.142 / 0.143	0.0627 / 0.0606
No. 124	0.0543 / 0.0540	0.106 / 0.105	0.110 / 0.108	0.146 / 0.145	0.0630 / 0.0620
No. 140	0.0529 / 0.0542	0.106 / 0.108	0.106 / 0.107	0.150 / 0.151	0.0624 / 0.0648
Mean (AV)	**0.0535 (0.0523)**	**0.105 (0.119)**	**0.108 (0.102)**	**0.145 (0.149)**	**0.0627 (0.0598)**
RSD (%)	**0.9**	**1.3**	**0.8**	**1.9**	**1.0**
S_{sam}^2 < (c) ?	2.1E-4 < 0.0040	0.0011 < 0.0079	2.5E-4 < 0.0081	0.0023 < 0.011	0 < 0.0047
Homogeneity test	**passed**	**passed**	**passed**	**passed**	**passed**

S_{sam}^2: between-samples STD

(c): Check Value (0.3* sigma-PT):

Homogeneity TEST

COMPULSORY Compounds

	Glyphosate	Matrine	Nicotine	Oxymatrine	Phosphonic acid
Sample	Concentration [mg/kg]				
No. 011	0.104 / 0.106	0.0934 / 0.0947	0.0883 / 0.0910	0.0733 / 0.0769	0.211 / 0.207
No. 034	0.104 / 0.102	0.0887 / 0.0942	0.0917 / 0.0957	0.0725 / 0.0705	0.209 / 0.212
No. 050	0.106 / 0.101	0.0886 / 0.0909	0.0923 / 0.0922	0.0727 / 0.0700	0.196 / 0.191
No. 073	0.105 / 0.106	0.0912 / 0.0894	0.0912 / 0.0921	0.0719 / 0.0697	0.200 / 0.210
No. 096	0.103 / 0.104	0.0885 / 0.0919	0.0932 / 0.0917	0.0767 / 0.0723	0.207 / 0.199
No. 112	0.102 / 0.108	0.0907 / 0.0903	0.0922 / 0.0926	0.0702 / 0.0719	0.194 / 0.195
No. 143	0.103 / 0.107	0.0905 / 0.0920	0.0899 / 0.0914	0.0712 / 0.0697	0.211 / 0.201
No. 156	0.106 / 0.104	0.0916 / 0.0936	0.0921 / 0.0902	0.0777 / 0.0738	0.203 / 0.206
No. 183	0.104 / 0.109	0.0922 / 0.0908	0.0966 / 0.0933	0.0671 / 0.0724	0.208 / 0.193
No. 200	0.103 / 0.099	0.0861 / 0.0914	0.0938 / 0.0936	0.0744 / 0.0729	0.207 / 0.211
Mean (AV)	**0.104 (0.102)**	**0.0910 (0.0873)**	**0.0923 (0.0877)**	**0.0724 (0.0681)**	**0.204 (0.202)**
RSD (%)	**1.5**	**1.7**	**1.7**	**3.0**	**2.8**
$S_{sam}^2 < (c)$?	0< 0.0078	1.9E-4< 0.0068	3.2E-5 < 0.007	0 .0015< 0.0054	0.0043 < 0.015
Homogeneity test	**passed**	**passed**	**passed**	**passed**	**passed**

S_{sam}^2: between-samples STD

(c): Check Value (0.3* sigma-PT):

Homogeneity TEST

OPTIONAL
Compounds

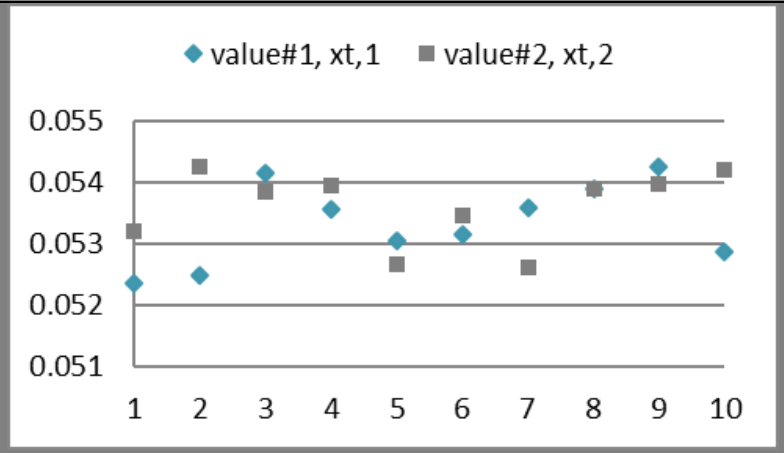
	Perchlorate	Trinexapac
Sample	**Concentration [mg/kg]**	
No. 001	0.0631 / 0.0587	0.108 / 0.101
No. 004	0.0605 / 0.0603	0.128 / 0.119
No. 020	0.0613 / 0.0607	0.115 / 0.097
No. 048	0.0618 / 0.0603	0.111 / 0.103
No. 067	0.0627 / 0.0628	0.107 / 0.101
No. 074	0.0573 / 0.0600	0.095 / 0.107
No. 89	0.0621 / 0.0618	0.113 / 0.106
No. 099	0.0619 / 0.0613	0.118 / 0.098
No. 124	0.0621 / 0.0602	0.105 / 0.085
No. 140	0.0616 / 0.0612	0.106 / 0.099
Mean (AV)	**0.0611 (0.0550)**	**0.106 (0.118)**
RSD (%)	**1.8**	**7%**
S_{sam}^2 < (c) ?	5.76E-4 < 0.0046	0.0040 < 0.0080
Homogeneity test	**passed**	**passed**

S_{sam}^2: between-samples STD
(c): Check Value (0.3* sigma-PT):

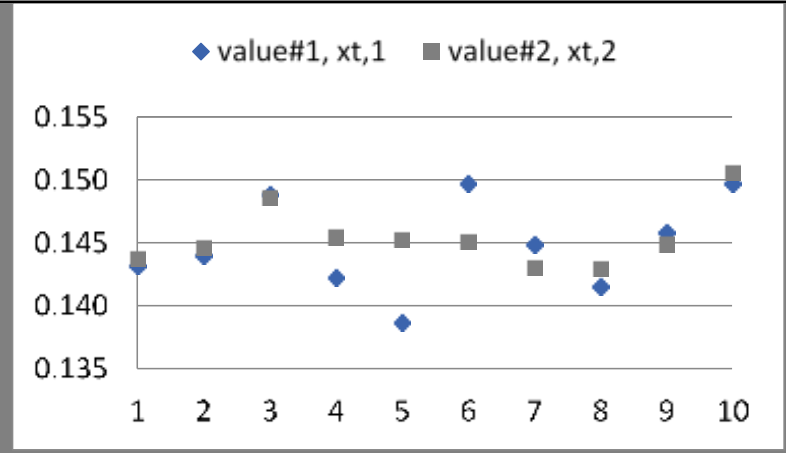
Homogeneity TEST

Distribution of results from 10 bottles (2 portions each), exemplary

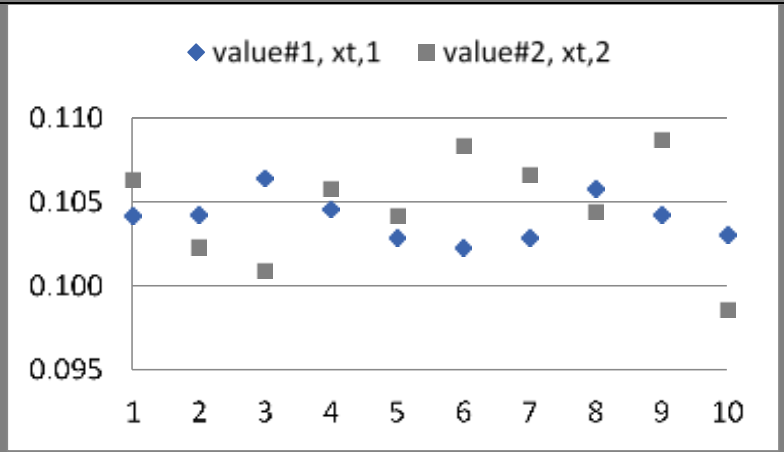
2,4-D



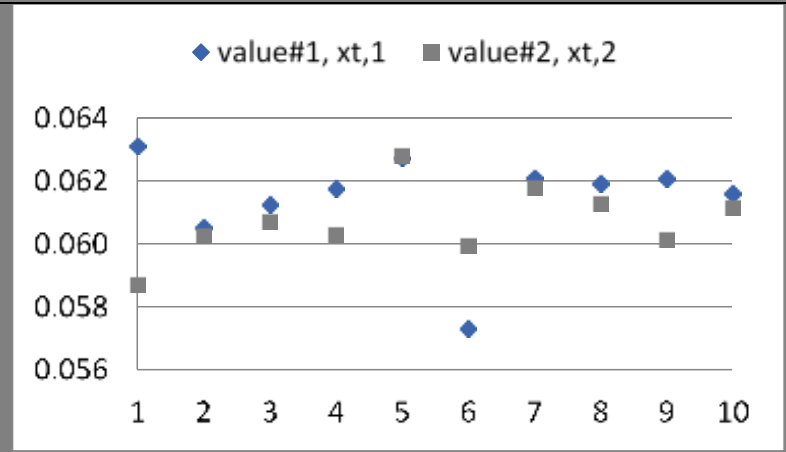
DDAC-C10



Glyphosate



Perchlorate



Stability TEST

COMPULSORY Compounds

	2,4-D			BAC-C14			Chlorate			DDAC-C10			Fluazifop		
Date of extraction	20.04.2023	25.05.2023	15.06.2023	20.04.2023	25.05.2023	15.06.2023	27.04.2023	25.05.2023	15.06.2023	20.04.2023	25.05.2023	15.06.2023	20.04.2023	25.05.2023	15.06.2023
No. 004	0.0534	0.0513	0.0552	0.105	0.105	0.0990	0.139	0.127	0.135	0.144	0.143	0.139	0.0636	0.0595	0.0616
No. 067	0.0528	0.0513	0.0548	0.103	0.109	0.0984	0.136	0.129	0.134	0.142	0.141	0.141	0.0623	0.0594	0.0607
No. 099	0.0539	0.0519	0.0548	0.104	0.106	0.0961	0.135	0.127	0.13	0.142	0.144	0.135	0.0616	0.0605	0.0616
Mean [mg/kg]	**0.0534**	**0.0515**	**0.0549**	**0.104**	**0.106**	**0.0978**	**0.136**	**0.128**	**0.133**	**0.143**	**0.143**	**0.138**	**0.0625**	**0.0598**	**0.0613**
% Diviation (vs. 1st Anaylsis)	-	-3.53%	2.95%	-	2.28%	-5.99%	-	-6.5%	-2.8%	-	-0.01%	-3.16%	-	-4.29%	-1.92%
Diff (mean)	-	**0.0019**	**0.0016**	-	**0.0024**	**0.0062**	-	**0.0088**	**0.0038**	-	**2E-05**	**0.0045**	-	**0.0027**	**0.0012**
0.3*FFP-SD		**0.0039**	**0.0039**		**0.0089**	**0.0089**		**0.012**	**0.012**		**0.011**	**0.011**		**0.0045**	**0.0045**
Stability test		**passed**	**passed**		**passed**	**passed**		**passed**	**passed**		**passed**	**passed**		**passed**	**passed**

	Glyphosate			Matrine			Nicotine			Oxymatrine			Phosphonic acid		
Date of extraction	27.04.2023	25.05.2023	15.06.2023	27.04.2023	25.05.2023	15.06.2023	27.04.2023	25.05.2023	15.06.2023	27.04.2023	25.05.2023	15.06.2023	27.04.2023	25.05.2023	15.06.2023
No. 004	0.103	0.100	0.107	0.0915	0.0986	0.0926	0.0937	0.0938	0.0937	0.0713	0.0697	0.0727	0.210		0.205
No. 067	0.104	0.0927	0.110	0.0902	0.0892	0.0888	0.0924	0.0896	0.0911	0.0711	0.0694	0.0710	0.203		0.207
No. 099	0.105	0.0984	0.106	0.0926	0.0961	0.0940	0.0911	0.0879	0.0937	0.0697	0.0716	0.0700	0.204		0.212
Mean [mg/kg]	**0.104**	**0.0970**	**0.107**	**0.0914**	**0.0946**	**0.0918**	**0.0924**	**0.0905**	**0.0929**	**0.0707**	**0.0702**	**0.0712**	**0.206**		**0.208**
% Diviation (vs. 1st Anaylsis)	-	-6.75%	3.34%	-	3.52%	0.42%	-	-2.13%	0.45%	-	-0.70%	0.76%	-		0.89%
Diff (mean)	-	**0.007**	**0.0035**	-	**0.0032**	**0.0004**	-	**0.0020**	**0.0004**	-	**0.0005**	**0.0005**	-		**0.0018**
0.3*FFP-SD		**0.0077**	**0.0077**		**0.0065**	**0.0065**		**0.0074**	**0.0074**		**0.0051**	**0.0051**			**0.015**
Stability test		**passed**	**passed**		**passed**	**passed**		**passed**	**passed**		**passed**	**passed**			**passed**

Instrumental issues, no measurement possible at that point

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

Stability TEST

OPTIONAL
Compounds

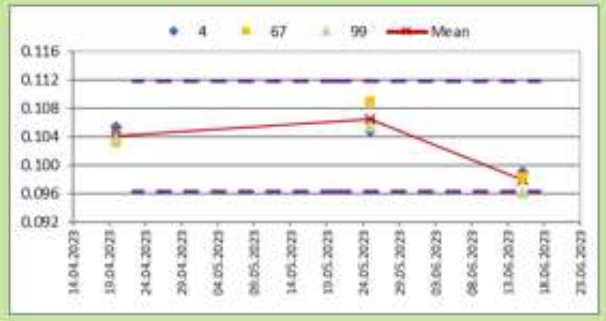
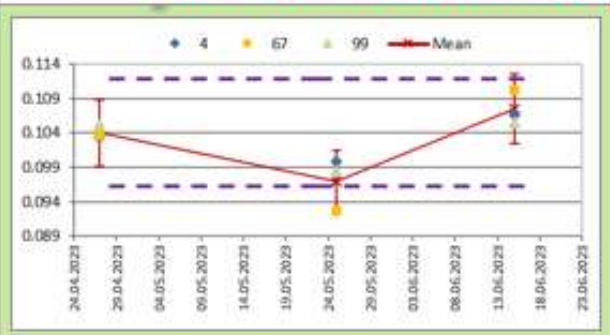
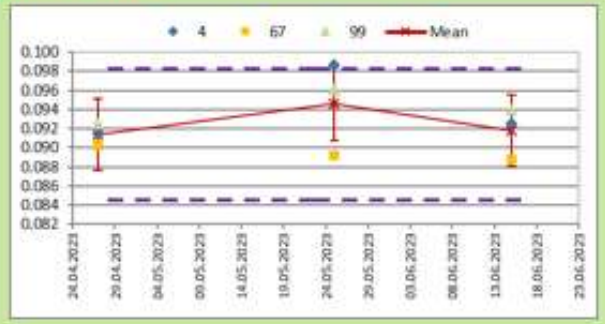
	Perchlorate			Trinexapac		
Date of extraction	27.04.2023	25.05.2023	15.06.2023	20.04.2023	25.05.2023	15.06.2023
No. 004	0.0604	0.0602	0.0603	0.1236	0.1115	0.1194
No. 067	0.0628	0.0604	0.0615	0.1083	0.1208	0.1087
No. 099	0.0616	0.0609	0.0613	0.1023	0.0999	0.1092
Mean [mg/kg]	**0.0616**	**0.0605**	**0.0610**	**0.1114**	**0.1107**	**0.1124**
% Diviation (vs. 1st Anaylsis)	-	-1.81%	-0.96%	-	-0.60%	0.89%
Diff (mean)	-	**0.0011**	**0.0006**	-	**0.0007**	**0.001**
0.3*FFP-SD		**0.0041**	**0.0041**		**0.0089**	**0.0089**
Stability test		**passed**	**passed**		**passed**	**passed**

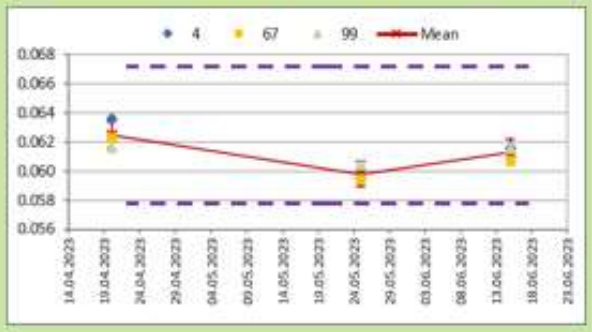
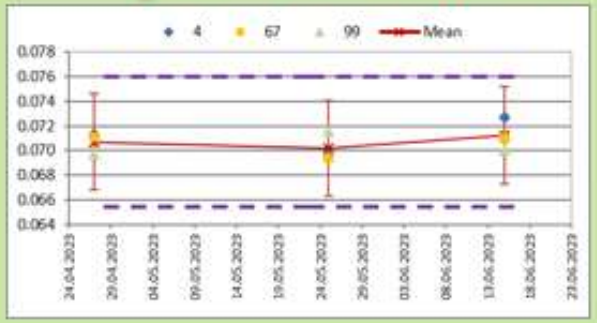
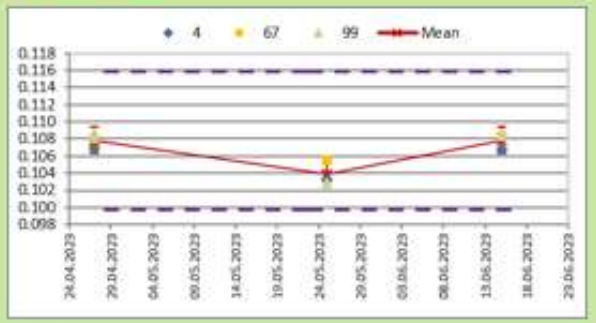
All stability test samples were extracted at the indicated day and measured alltogether at the end.

Stability TEST

Standard Deviation derived from quintuplicate injection of one sample

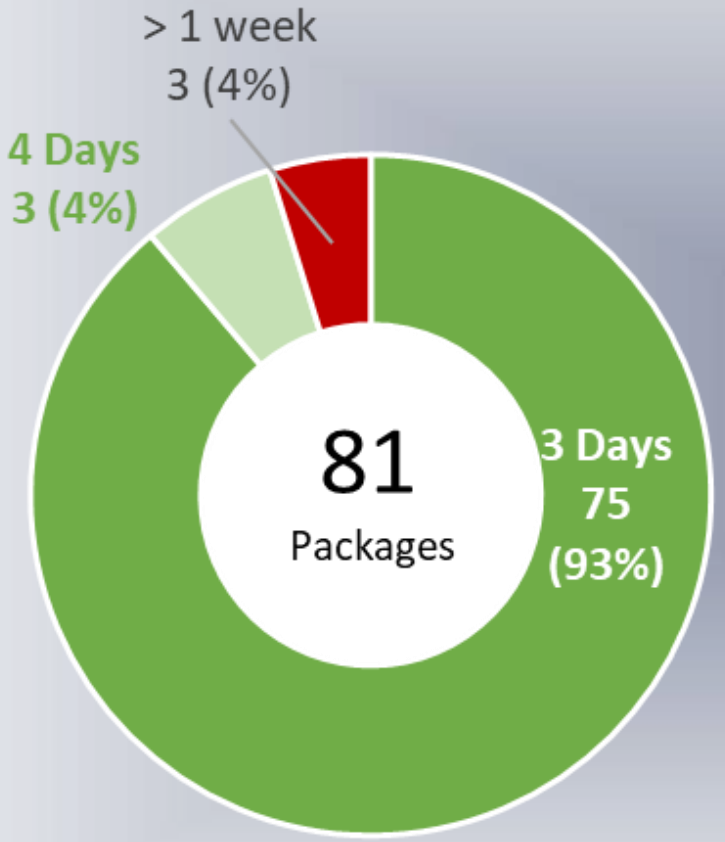
Mean values within range, individual values outside

EXAMPLES	BAC C14	Glyphosate	Matrine
	---- limits for acceptable mean values	RSD % of three injections of one sample	
MEAN within range			

EXAMPLES	Fluazifop	Oxymatrine	Chlorate
	---- limits for acceptable mean values	RSD % of three injections of one sample	
ALL within range			

Stability during shipping

Shipment Duration



Dispatched on Friday without cooling

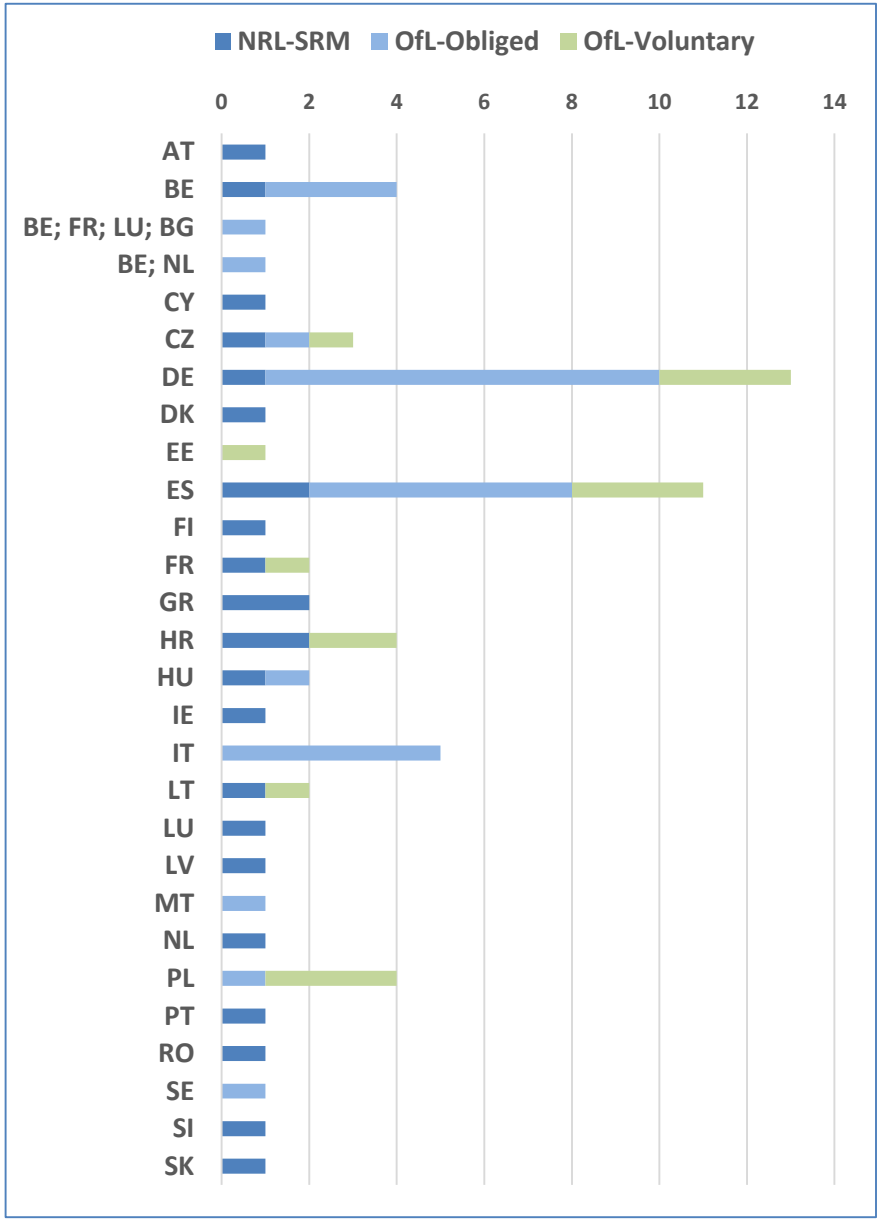
- **Arrival on Mon. (3 days): 93 %**
- **Arrival on Tue. (4 days): 4 %**
  - 3 EU (2x ES, 1x CY): remote Location
- **All packages to EU and EFTA-labs arrived within 4 days.**
- **≥ 1 Week: EU Candidate and 3rd Countries**
  - VN (7 days): was kept frozen at local DHL
  - RS (13 days)
  - RS (> 1 month): (counted as non-participating)
- **Test material for 1 participating labs in Latin America was handed over at LAPRW**

Participating labs / countries

		Labs submitting results	Registered WITHOUT submitting results
EU OfLs		69	2* + 1‡ + 2
EFTA OfLs		2	0
3rd Countries + EU Candidates		4	2
	SUM	75	7

Non-participating EU OfLs:
2* labs informed during SRM18 that their instument was broken,
1‡ lab informed after the PT that the standards were delivered too late to complete the PT,
2 labs have not yet stated their reasons for non-submission.

Participating labs / countries



EFTA-Countries	Participated in EUPT-SRM18
CH	1
NO	1
EFTA-Total	2

EU Candidate & 3rd countries	Participated in EUPT-SRM18
RS	1
UY	1
VN	1
UK	1
EU Cand. & 3rd C. Total	4

7 labs having not submitting results not shown.

No NRL-SRM participant from 3 countries:

- EE (major lab Re-organisation)
- IT (Failed to submit results)
- SE (Only few compounds of TPL covered)
- MT (no lab, subcontracting NRL to ?)

Frequency of analysis

COMPULSORY, OPTIONAL and Extra Compounds

Percentage based on 71 (69 EU + 2 EFTA) labs registered and submitting results

Present in Test Material — No. of Labs Analysed

Glyphosate	64
2,4-D (free acid)	60
Fluazifop (free acid)	59
Chlorate (anion)	48
DDAC-C10 chloride	46
Perchlorate	46
BAC-C14 chloride	45
Phosphonic acid	45
Nicotine	42
Matrine	40
Oxymatrine	36
Trinexapac (free acid)	31

NOT Present in Test Material — No. of Labs Analysed

Haloxyfop (free acid)	60
Chlormequat chloride	59
Mepiquat chloride	57
MCPA (free acid)	54
Quizalofop (free acid)	52
Fosetyl	51
AMPA	51
BAC-C12 chloride	45
N-Acetyl glyphosate	33
Chloridazon, desphenyl-	26

Extra Analytes present in Natural Content — No. of Labs Analysed

Bromide (anion)	34
Copper	12

≥ 80 %
50 – 79 %
25 – 49 %
< 25 %

EU+EFTA

False negatives

COMPULSORY Compounds

EU+EFTA

False Negatives (FN) 14

	Analyte	MRRL [mg/kg]	AV [mg/kg]	No. of FNs	Lab Code	RL [mg/kg]	Judgement
COMPULSORY	BAC-C14 chloride	0.01	0.119	3	3	0.01	FN
					58	0.01	FN
					77	0.01	FN
	Chlorate (anion)	0.01	0.102	3	18	0.01	FN
					45	0.01	FN
					69	0.01	FN
	DDAC-C10 chloride	0.01	0.149	2	3	0.01	FN
					77	0.01	FN
	Fluazifop (free acid)	0.01	0.0598	1	58	0.01	FN
	Glyphosate	0.01	0.102	1	45	0.01	FN
	Matrine	0.01	0.0873	1	52	0.05	FN
	Nicotine	0.01	0.0877	2	69	0.01	FN
					82	0.1	FN* (RL > AV)
	Phosphonic acid	0.03	0.202	1	45	0.03	FN

False negatives

OPTIONAL Compounds

EU+EFTA

False Negatives (FN) 14

	Analyte	MRRL [mg/kg]	AV [mg/kg]	No. of FNs	Lab Code	RL [mg/kg]	Judgement
COMPULSORY	Perchlorate	0.01	0.0550	4	11	0.01	FN
					45	0.01	FN
					64	0.01	FN
					69	0.01	FN
	Trinexapac (free acid)	0.01	0.118	10	3	0.01	FN
					5	0.01	FN
					16	0.01	FN
					26	0.01	FN
					45	0.01	FN
					57	0.01	FN
					61	0.01	FN
					69	0.01	FN
					71	0.01	FN
					79	0.01	FN

5x „Wrong Standard used (Trinexapac-ethyl)
1x „Lack of Experience“
1x „Transcription Error“
3x No answer yet

False Negatives by lab

Lab-Co	Trinexapac (free acid)	Fluazifop (free acid)	BAC-C14 chloride	DDAC-C10 chloride	Chlorate (anion)	Perchlorate	Phosphonic acid	Glyphosate	Matrine	Oxymatrine	Nicotine	Overall
45*	1				1	1	1	1				5
69	1				1	1					1	4
70								1	1	1		3
3	1		1	1								3
77			1	1								2
58		1	1									2
71	1											1
82*											1	1
79	1											1
26	1											1
5	1											1
52									1			1
16	1											1
11*						1						1
18					1							1
57*	1											1
61	1											1
64						1						1

(False) Negatives

Extra Compounds, Present (natural content)

EU+EFTA

	Analyte	MRRL [mg/kg]	not detected LabCode	RL [mg/kg]
Extra Analytes	Bromide (anion)	none	5	0.5
			11	0.5
			14	1
			15	0.5
			17	0.5
			26	5
			32	2
			33	0.5
			37	1
			38	0.5
			41	0.2
			42	0.5
			44	0.5
			45	0.5
			48	1
			50	2.5
			51	0.5
			52	2.5
			54	0.5
			55	0.5
			57	0.5
			62	0.5
			63	0.5
			66	0.5
			67	0.05
			73	0.5
			74	1
			78	0.5
	Copper	none	17	0.5
			74	1

Copper:

2x FNs

10 numerical results (median 0.048 mg/kg)

No MRL established

Bromide:

28x “FNs”

6 numerical results (median 0.09 mg/kg)

MRL: 0.05* (should be higher)

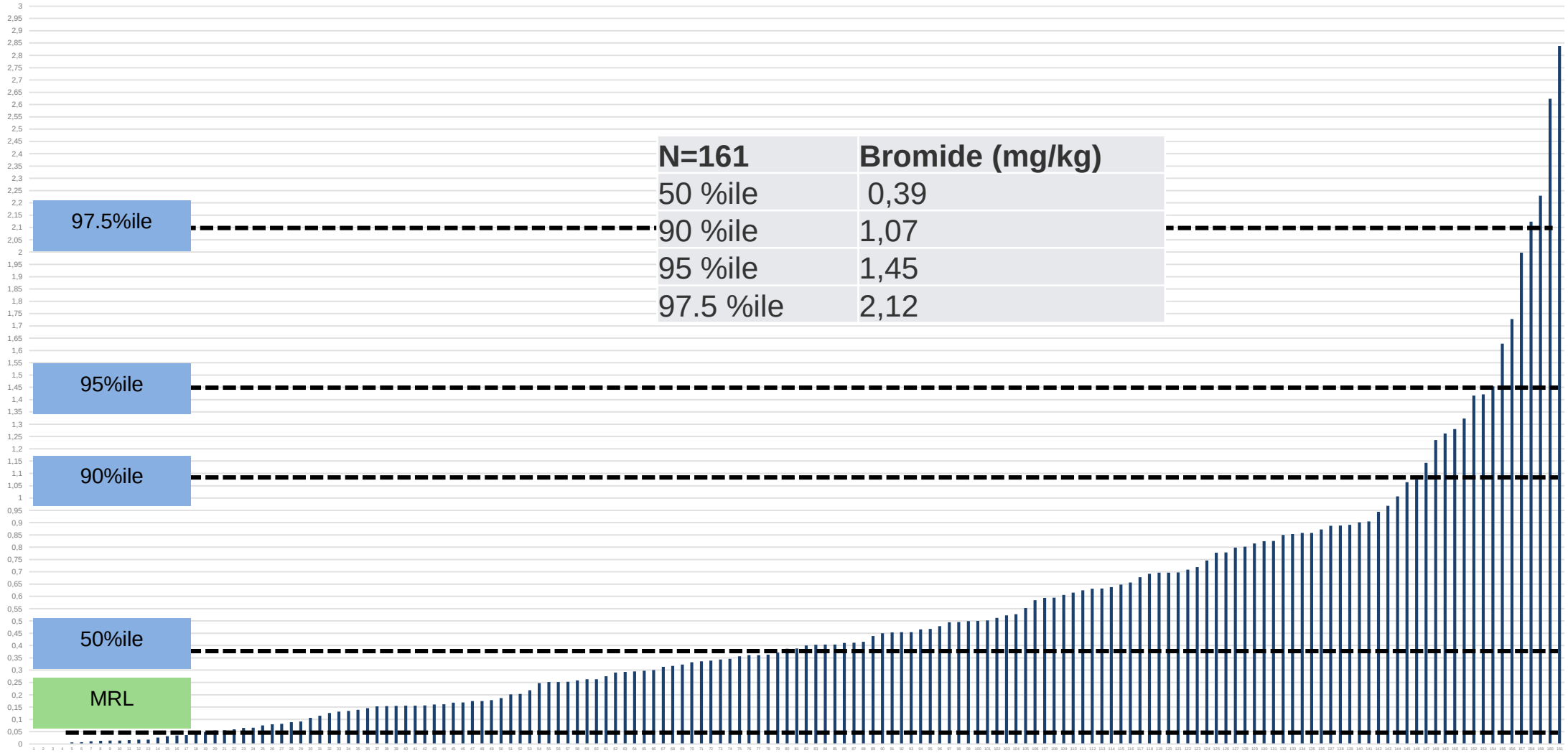
(if based on OfL-LOQs should be e.g. 0.5* mg/kg)

(if based on real levels should be at 1.5 or 2* mg/kg)

RLs (mg/kg)	No Labs
0,05	1
0,2	1
0,5	18
1	4
2	1
2,5	2
5	1
SUM	28

Statistical establishment of AVs for Bromide-ion and Cu not possible.

Bromide Levels in Honey



N=161	Bromide (mg/kg)
50 %ile	0,39
90 %ile	1,07
95 %ile	1,45
97.5 %ile	2,12

EU+EFTA

No False Positive Results in the EUPT-SRM18!

RESULTS OVERVIEW

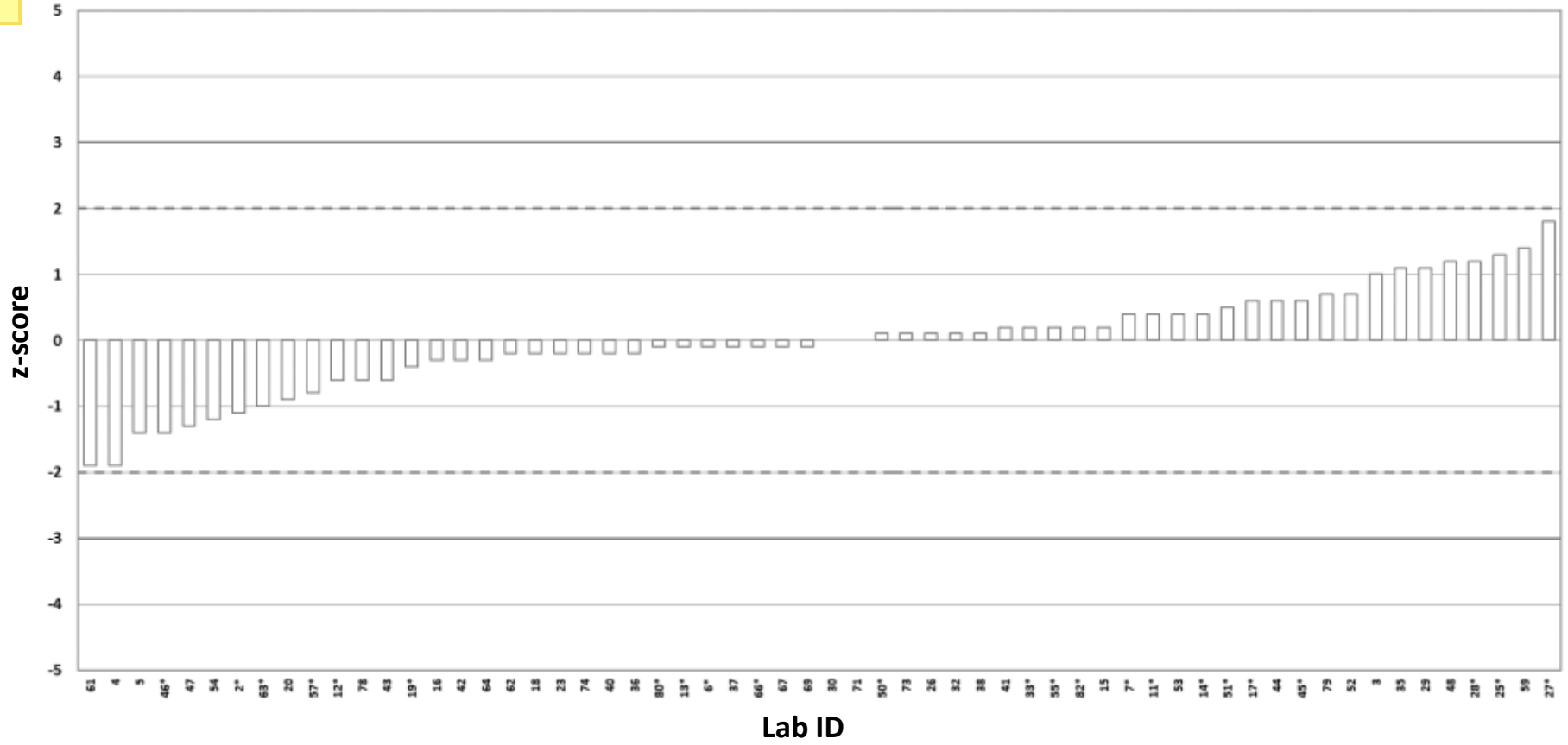
COMPULSORY

Compounds

2,4-D

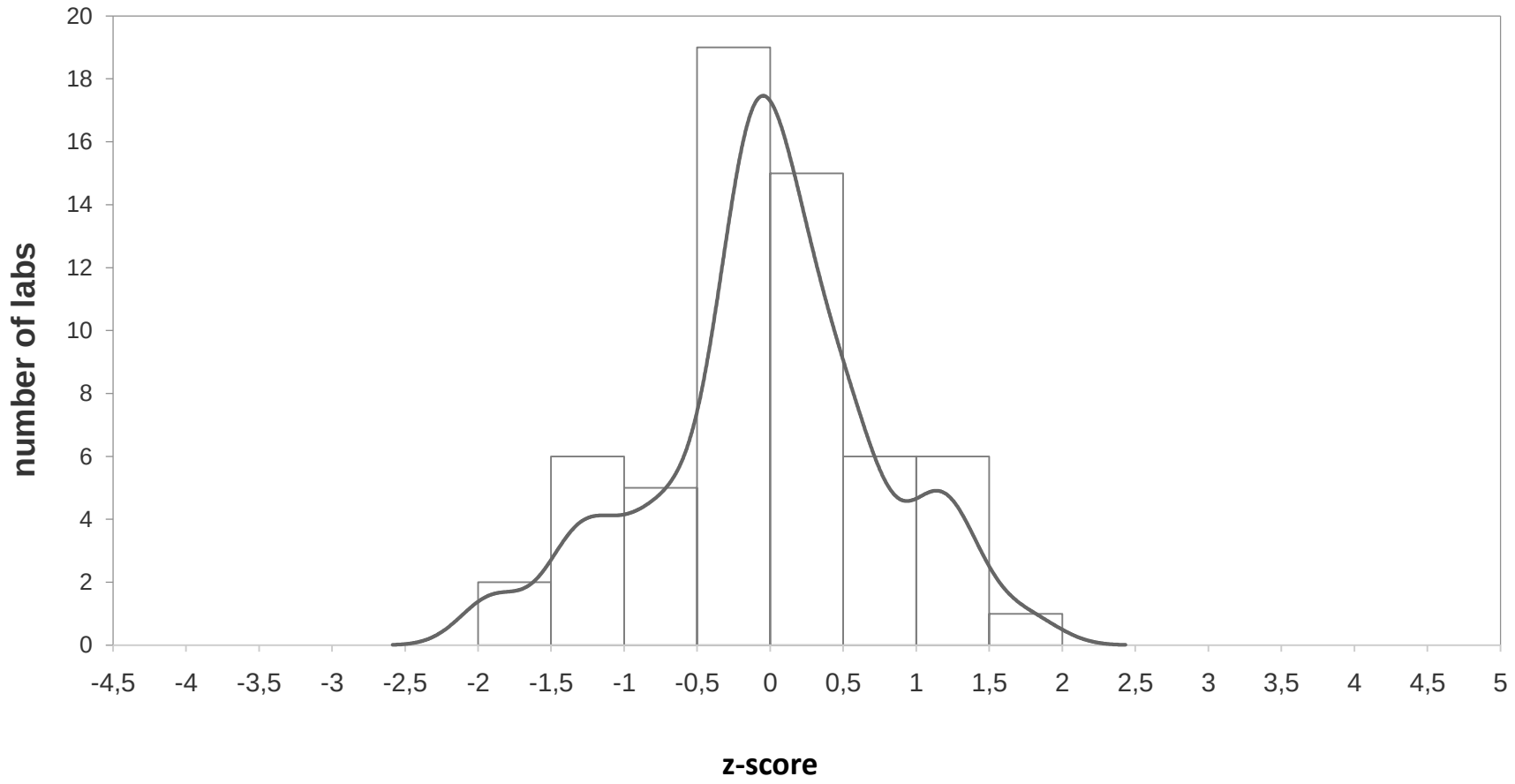
Results	60
False Neg.	0
AV	0.0523 [mg/kg]
CV*	18.9%
MRRL	0.01 [mg/kg]
UAV-test	passed

	|z-score| ≤ 2	Acceptable	60	(100%)
	2 < |z-score| < 3	Questionable	0	(0%)
	|z-score| ≥ 3	Unacceptable	0	(0%)
	False Negative		0	(0%)



2,4-D

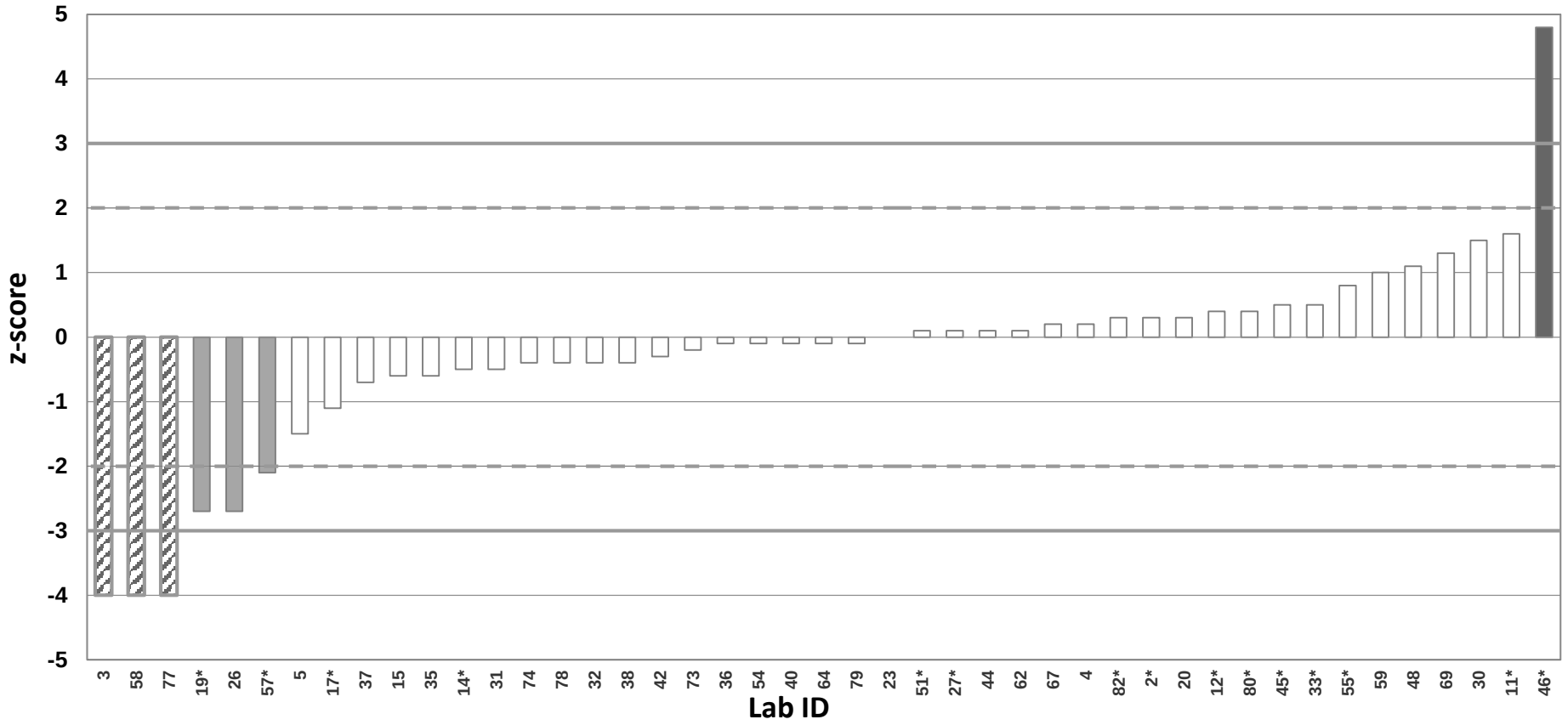
Results	60
False Neg.	0
AV	0.0523 [mg/kg]
CV*	18.9%
MRRL	0.01 [mg/kg]
UAV-test	passed



BAC-C14

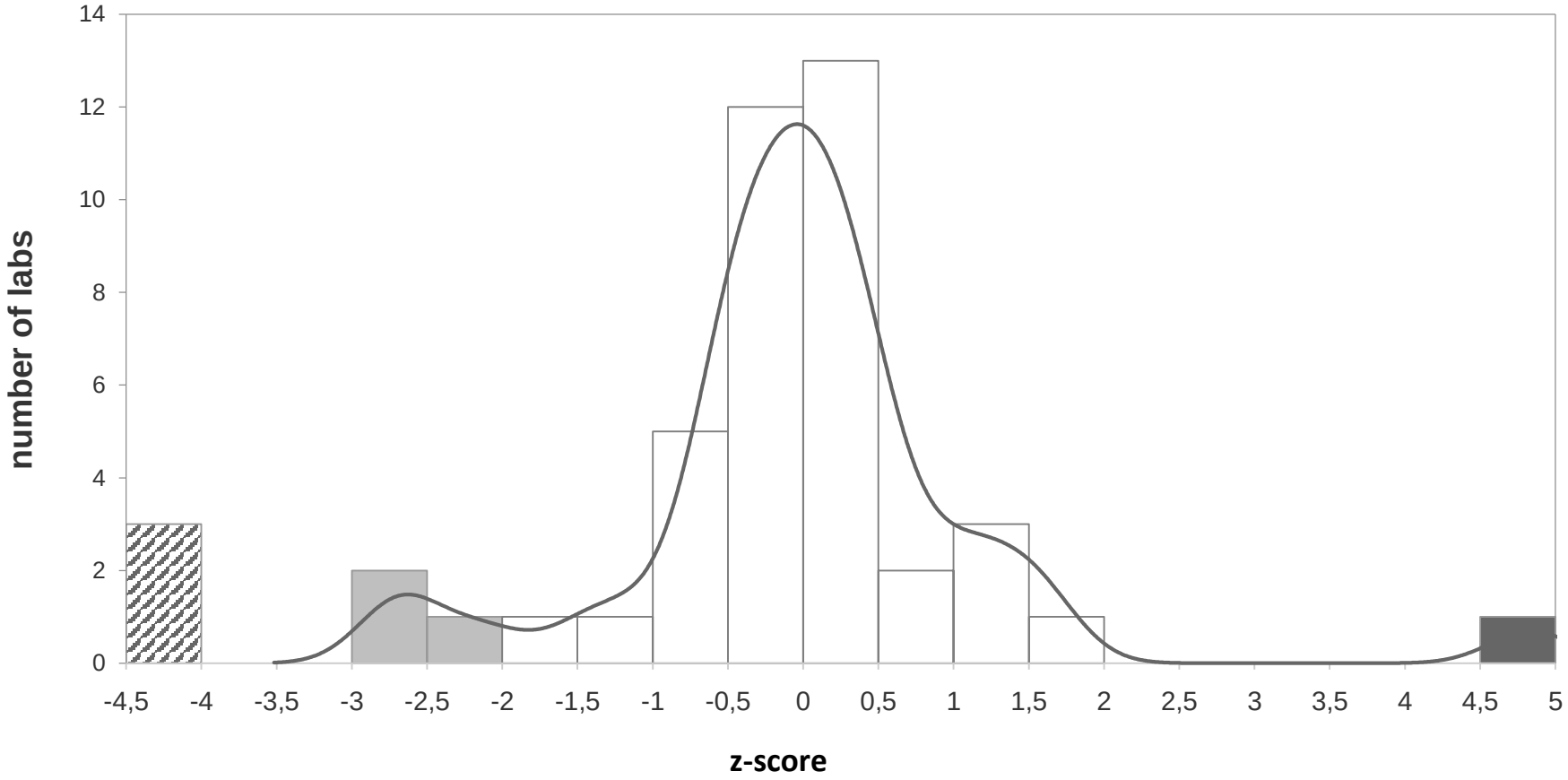
Results	42
False Neg.	3
AV	0.119 [mg/kg]
CV*	19.0 %
MRRL	0.01 [mg/kg]
UAV-test	passed

	|z-score| ≤ 2	Acceptable	38	(84%)
	2 < |z-score| < 3	Questionable	3	(7%)
	|z-score| ≥ 3	Unacceptable	1	(2%)
	False Negative		3	(7%)



BAC-C14

Results	42
False Neg.	3
AV	0.119 [mg/kg]
CV*	19.0 %
MRRL	0.01 [mg/kg]
UAV-test	passed

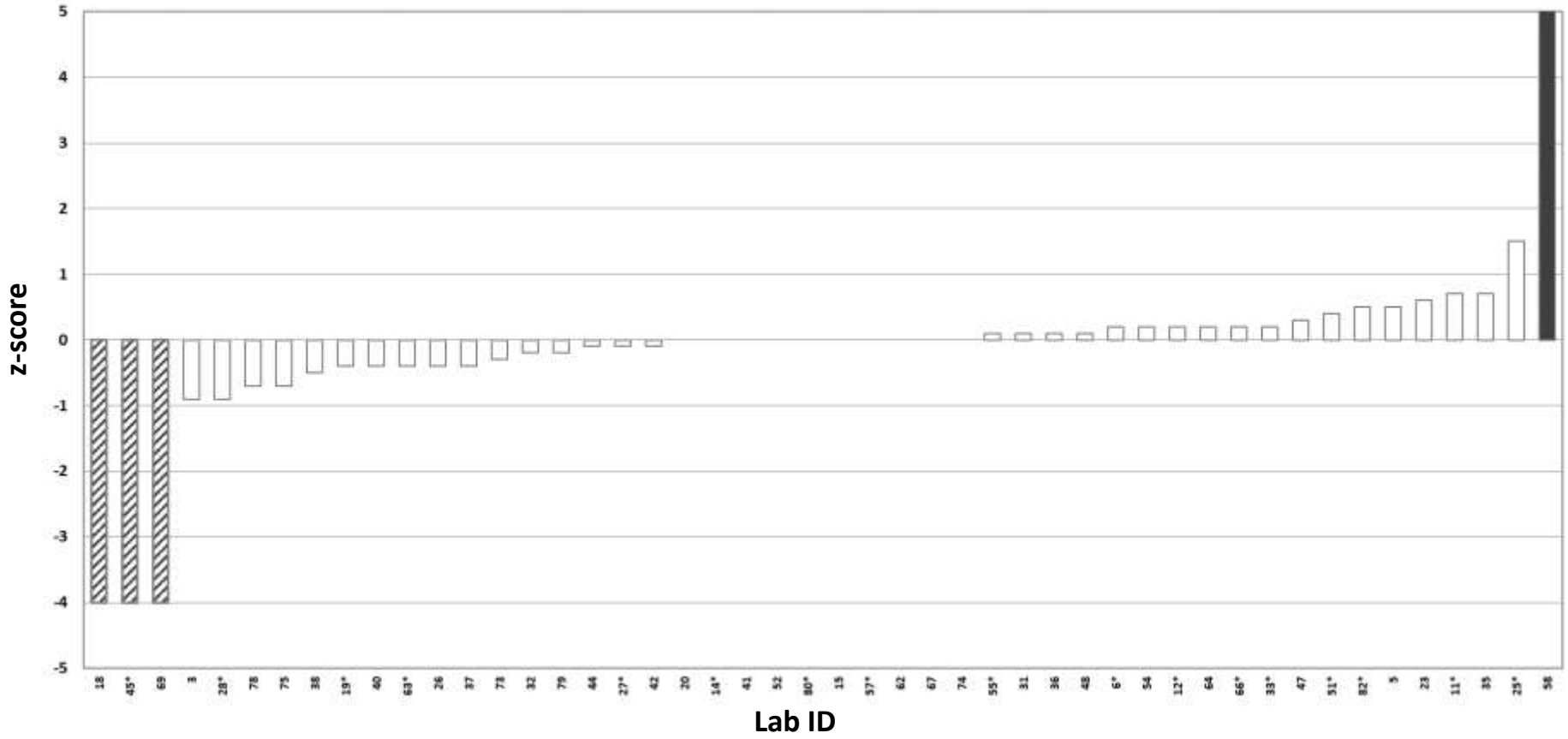


Chlorate

Results	45
False Neg.	3
AV	0.102 [mg/kg]
CV*	9.8 %
MRRL	0.01 [mg/kg]
UAV-test	passed

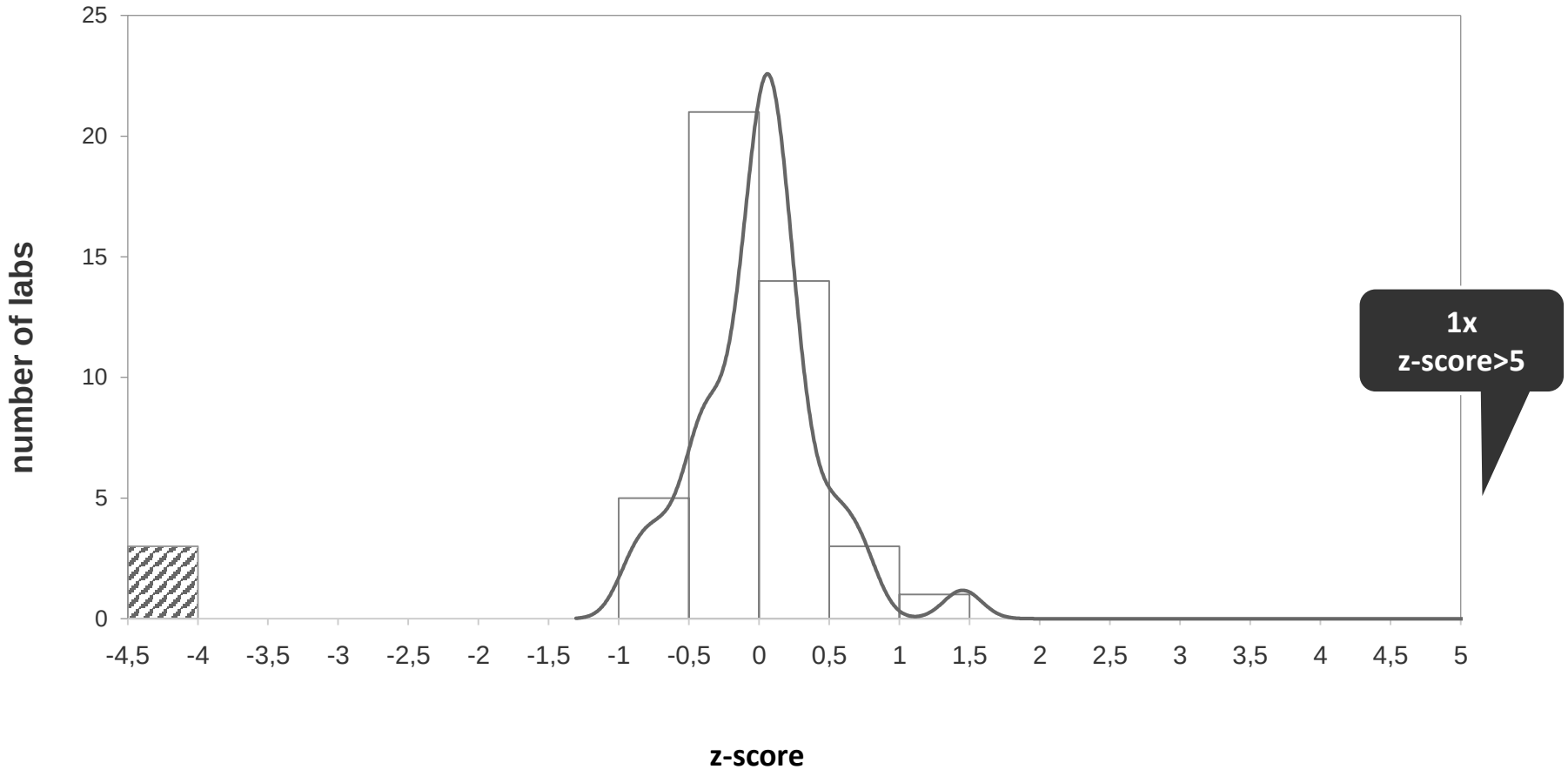
	|z-score| ≤ 2	Acceptable	44	(92%)
	2 < |z-score| < 3	Questionable	0	(0%)
	|z-score| ≥ 3	Unacceptable	1	(2%)
	False Negative		3	(6%)

1x>5



Chlorate

Results	45
False Neg.	3
AV	0.102 [mg/kg]
CV*	9.8 %
MRRL	0.01 [mg/kg]
UAV-test	passed



Chlorate

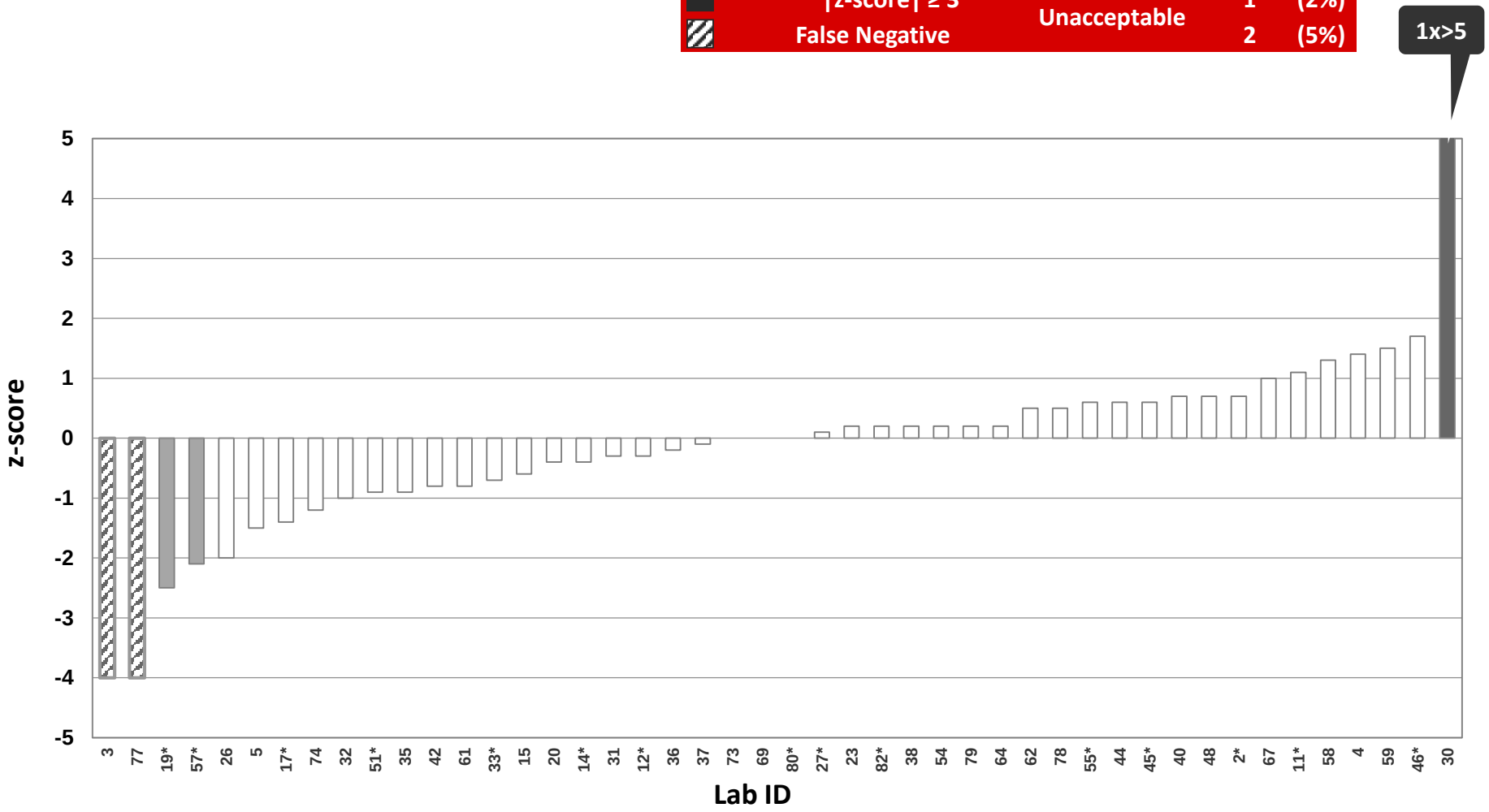
Impact of using ILIS

CHLORATE	Total	ILIS-Yes	ILIS-No
Values	47	28	19
Median	0,103	0,103	0,102
Robust Mean	0,102	0,102	0,102
CV*	10%	8%	14%
RSD	28%	9%	43%

DDAC-C10

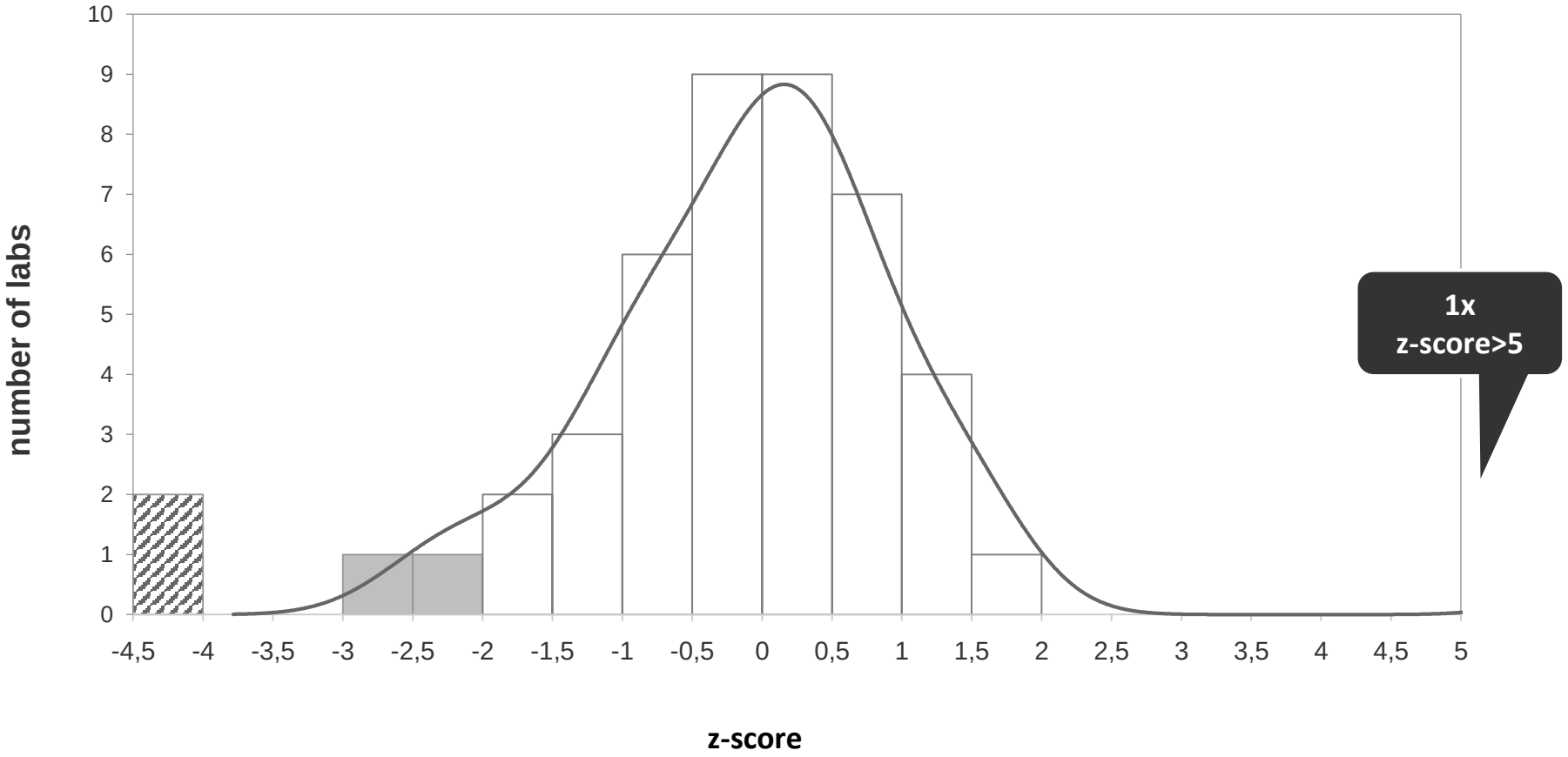
Results	44
False Neg.	2
AV	0.149 [mg/kg]
CV*	25.0 %
MRRL	0.01 [mg/kg]
UAV-test	passed

	|z-score| ≤ 2	Acceptable	41	(89%)
	2 < |z-score| < 3	Questionable	2	(4%)
	|z-score| ≥ 3	Unacceptable	1	(2%)
	False Negative		2	(5%)



DDAC-C10

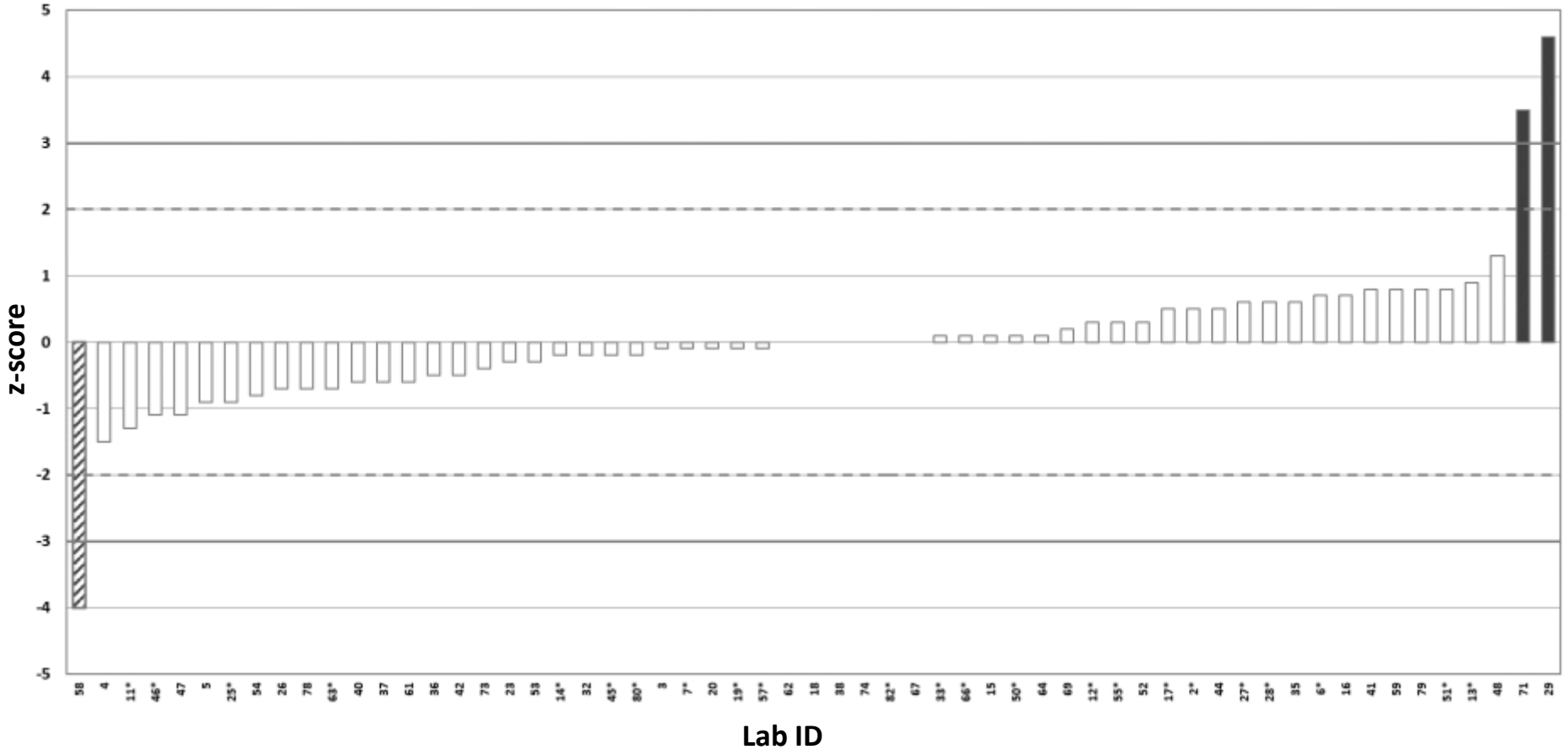
Results	44
False Neg.	2
AV	0.149 [mg/kg]
CV*	25.0 %
MRRL	0.01 [mg/kg]
UAV-test	passed



Fluazifop free acid

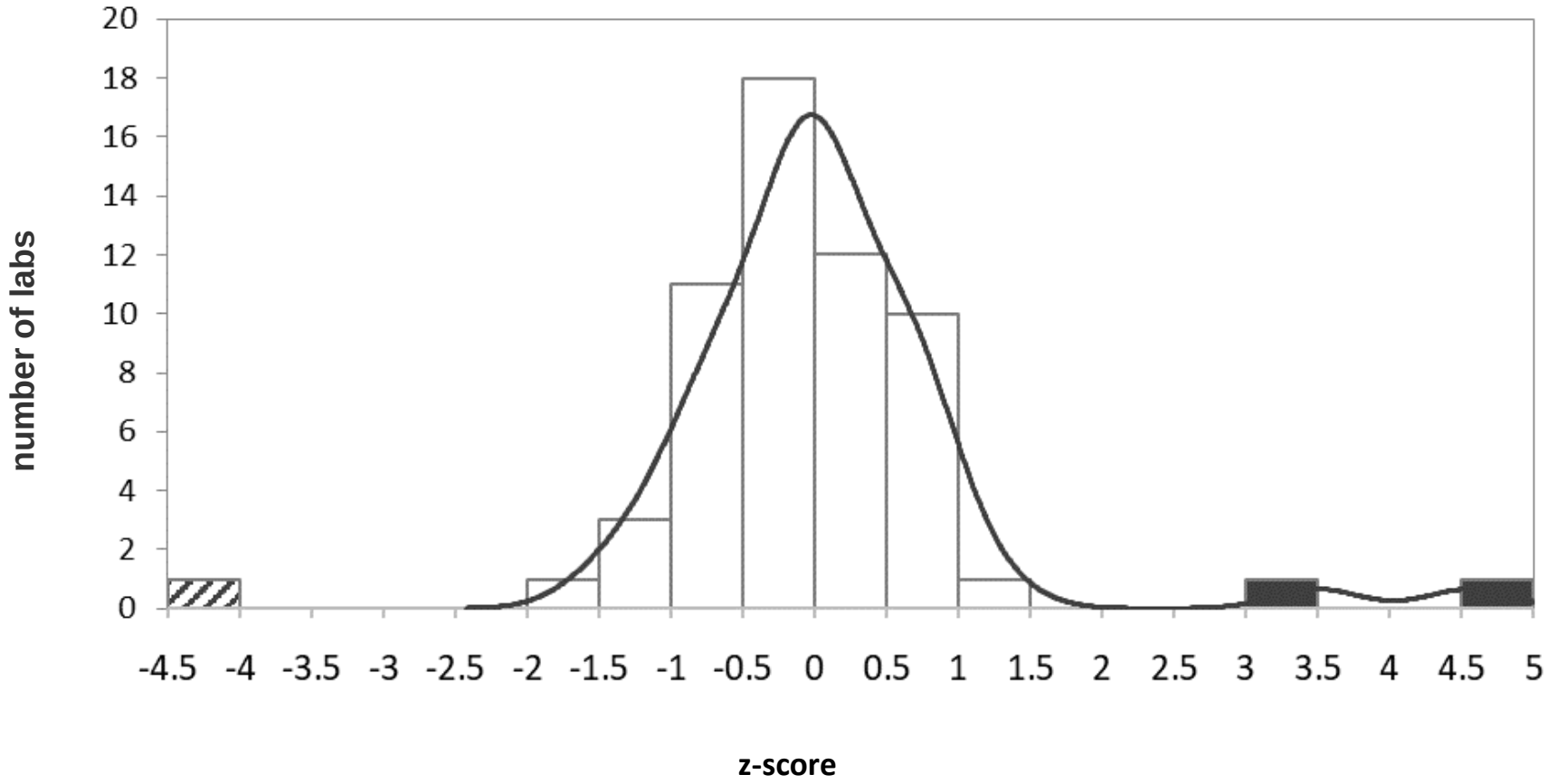
Results	58
False Neg.	1
AV	0.0598 [mg/kg]
CV*	16.5 %
MRRL	0.01 [mg/kg]
UAV-test	passed

	|z-score| ≤ 2	Acceptable	56	(95%)
	2 < |z-score| < 3	Questionable	0	(0%)
	|z-score| ≥ 3	Unacceptable	2	(3%)
	False Negative		1	(2%)



Fluazifop free acid

Results	58
False Neg.	1
AV	0.0598 [mg/kg]
CV*	16.5 %
MRRL	0.01 [mg/kg]
UAV-test	passed

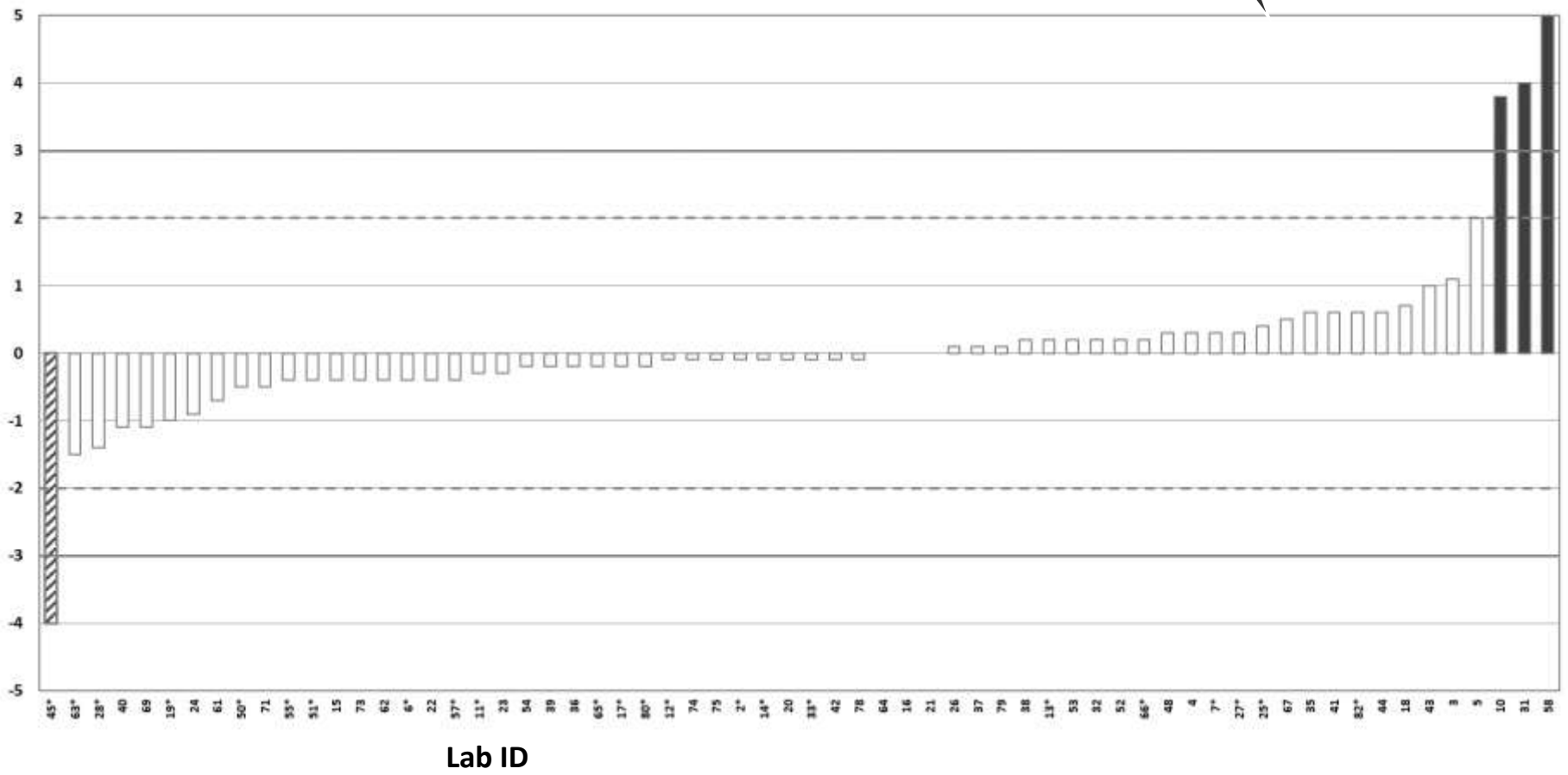


GLYPHOSATE

Results	63
False Neg.	1
AV	0.102 [mg/kg]
CV*	12.8 %
MRRL	0.01 [mg/kg]
UAV-test	passed

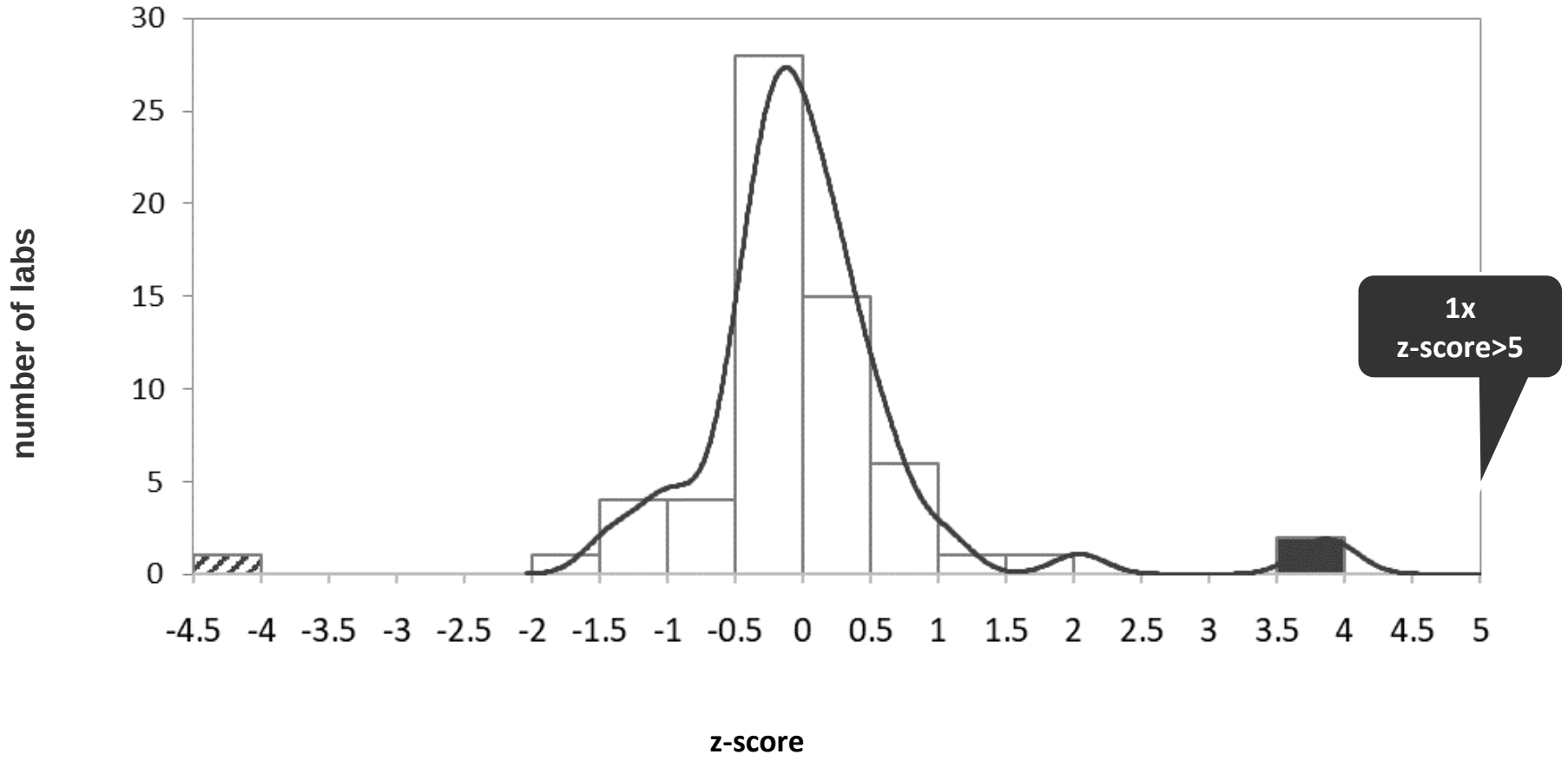
|z-score| ≤ 2	Acceptable	60	(77%)
2 < |z-score| < 3	Questionable	0	(9%)
|z-score| ≥ 3	Unacceptable	3	(13%)
False Negative		1	(1%)

1x z>5



Glyphosate

Results	63
False Neg.	1
AV	0.102 [mg/kg]
CV*	12.8 %
MRRL	0.01 [mg/kg]
UAV-test	passed

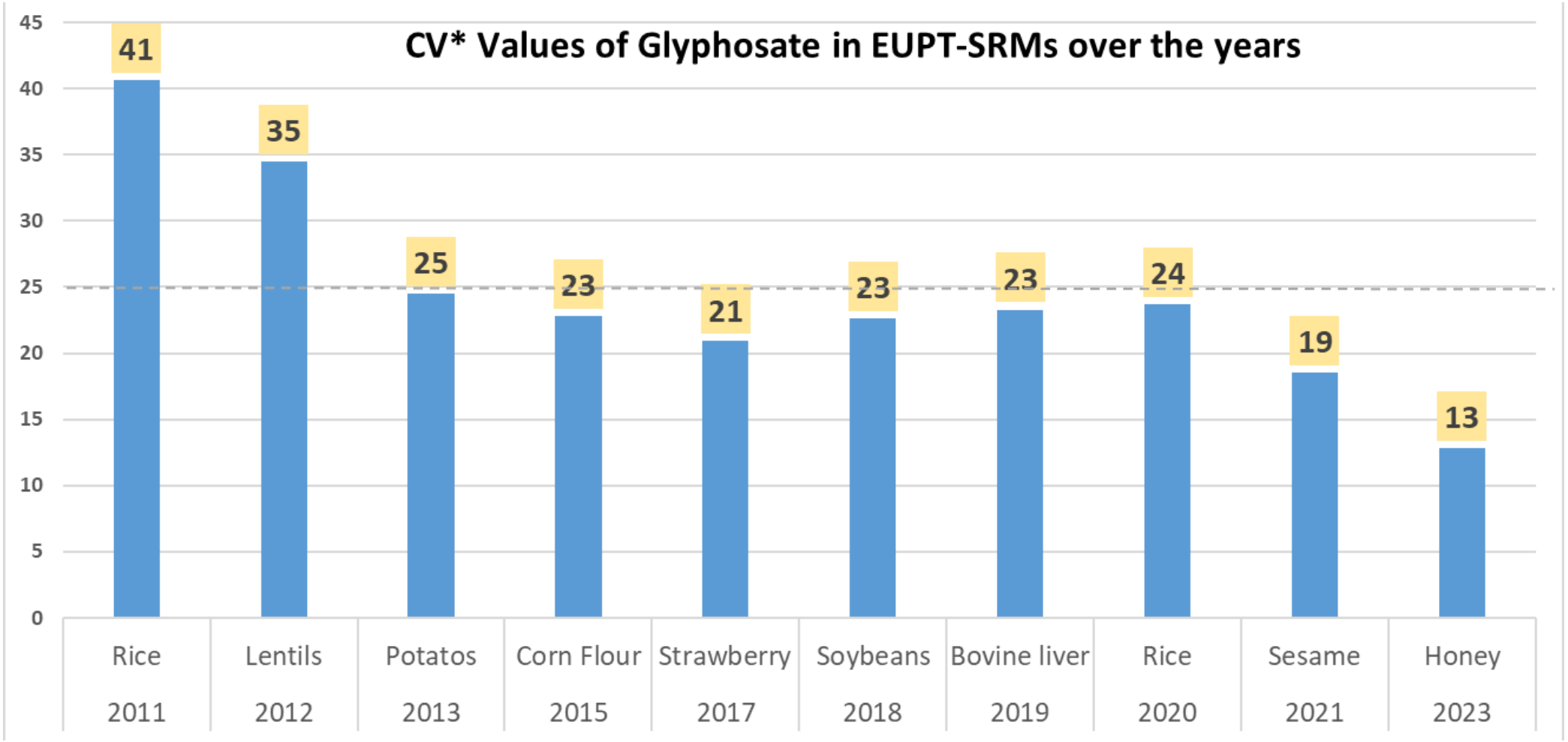


Glyphosate

Impact of using ILIS

GLYPHOSATE	Total	ILIS-Yes	ILIS-No
Values	66	46	20
Median	0,100	0,100	0,100
Robust Mean	0,102	0,102	0,100
CV*	**13%**	**13%**	**16%**
RSD	**30%**	**23%**	**43%**

Long-term Performance - Glyphosate



EURL-SRM

Glyphosate and Chlormequate (since SRM4)

Long-term Performance - Glyphosate

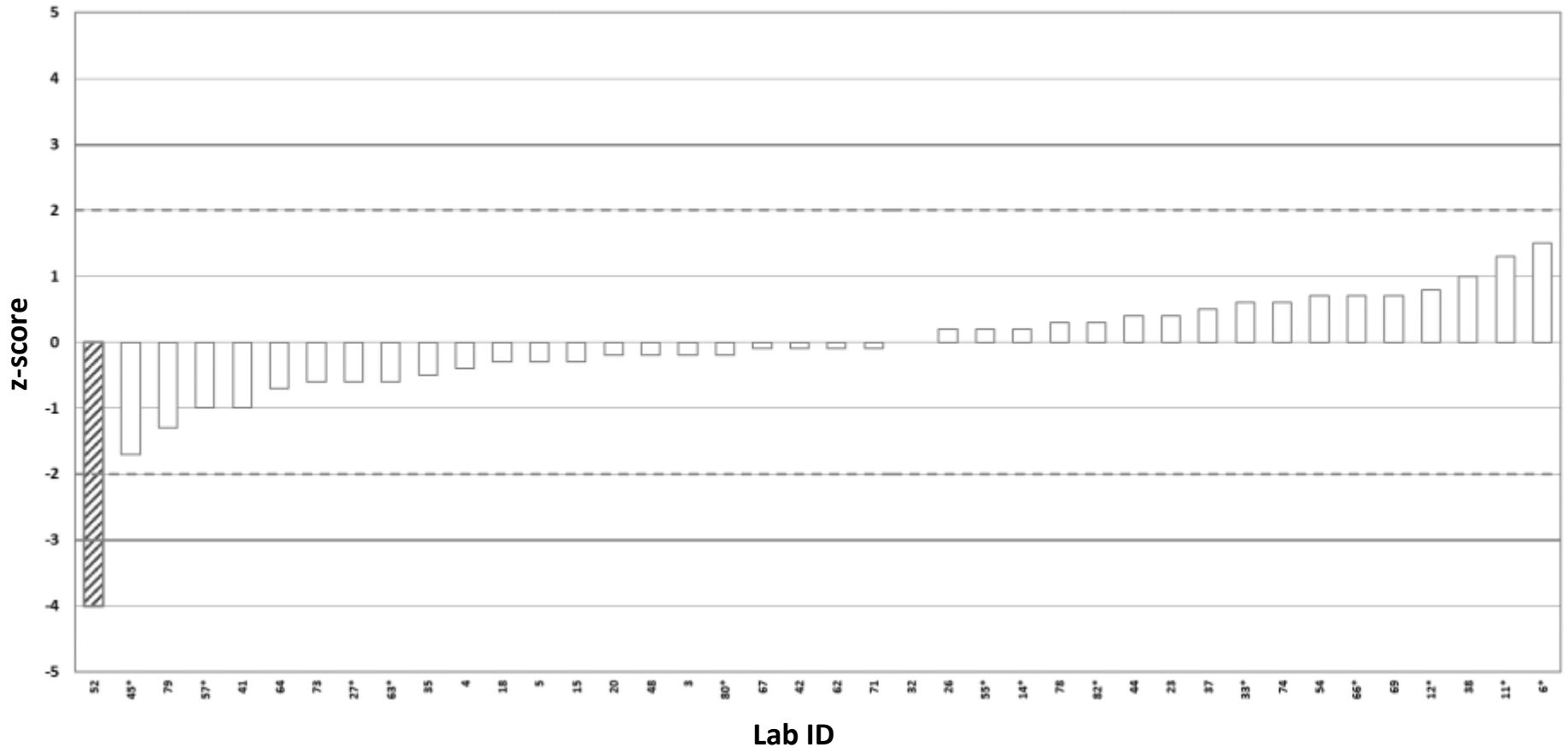
	SRM4	SRM6	SRM7	SRM8	SRM10	SRM12	SRM13	SRM14	SRM15	SRM16	SRM18
Matrix	Oats	Rice	Lentils	Potatoes	Maiz	Straw-berries	Soy-beans	Liver	Rice	Sesame	Honey
Glyphosate											
No. Results	6	34	39	45	62	86	83	43	84	88	66
% of Particip.	13%	34%	35%	41%	60%	67%	76%	75%	78%	88%	90%
CV* [%]	--	40.6%	34.5%	24.5%	22.8%	20.9%	22.6%	23.3%	23.7%	18.5%	12.8%

Avg CV*= 22.7 %

Matrine

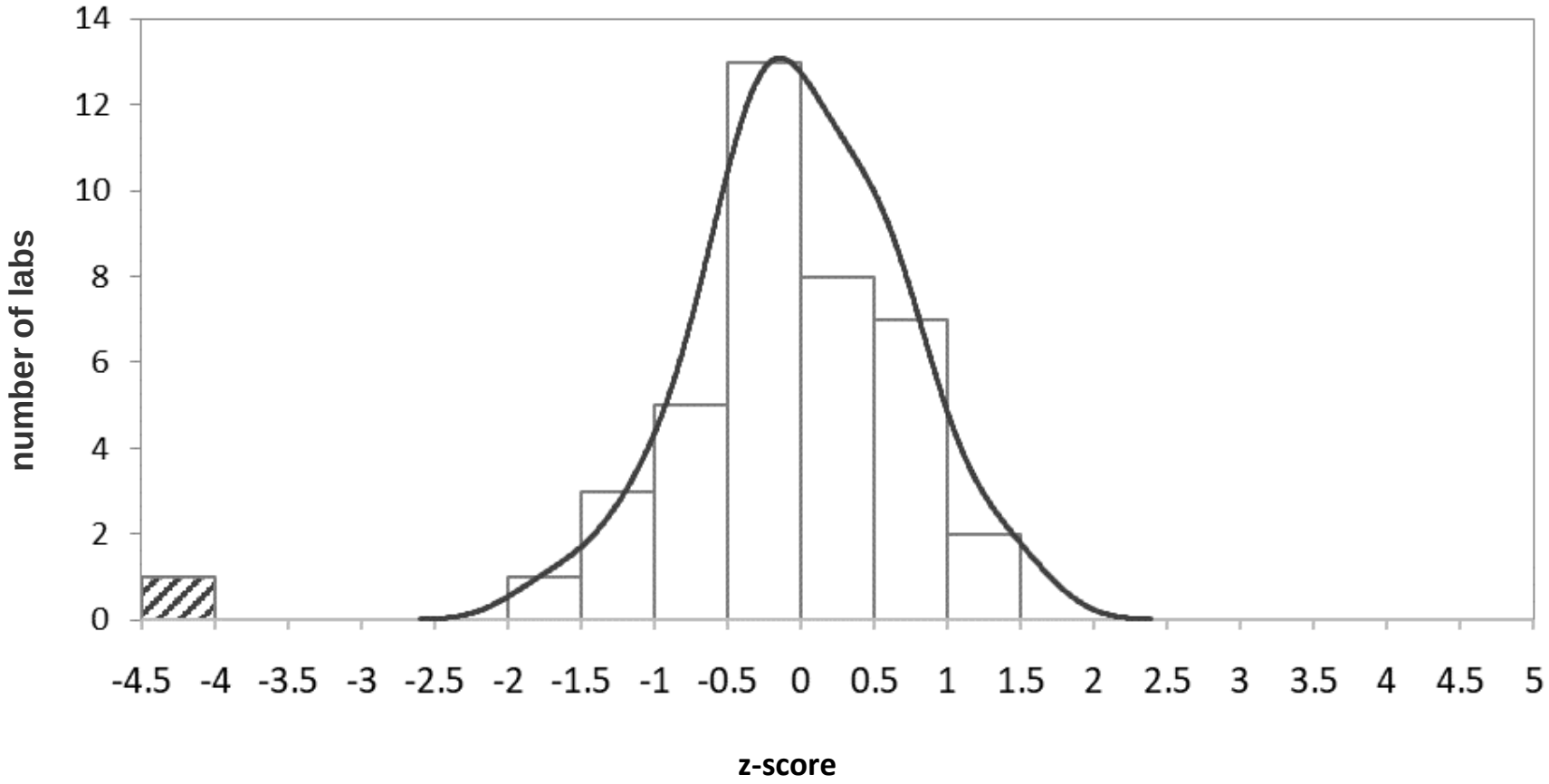
Results	39
False Neg.	1
AV	0.0873 [mg/kg]
CV*	16.9 %
MRRL	0.01 [mg/kg]
UAV-test	passed

	|z-score| ≤ 2	Acceptable	39	(97%)
	2 < |z-score| < 3	Questionable	0	(0%)
	|z-score| ≥ 3	Unacceptable	0	(0%)
	False Negative		1	(3%)



Matrine

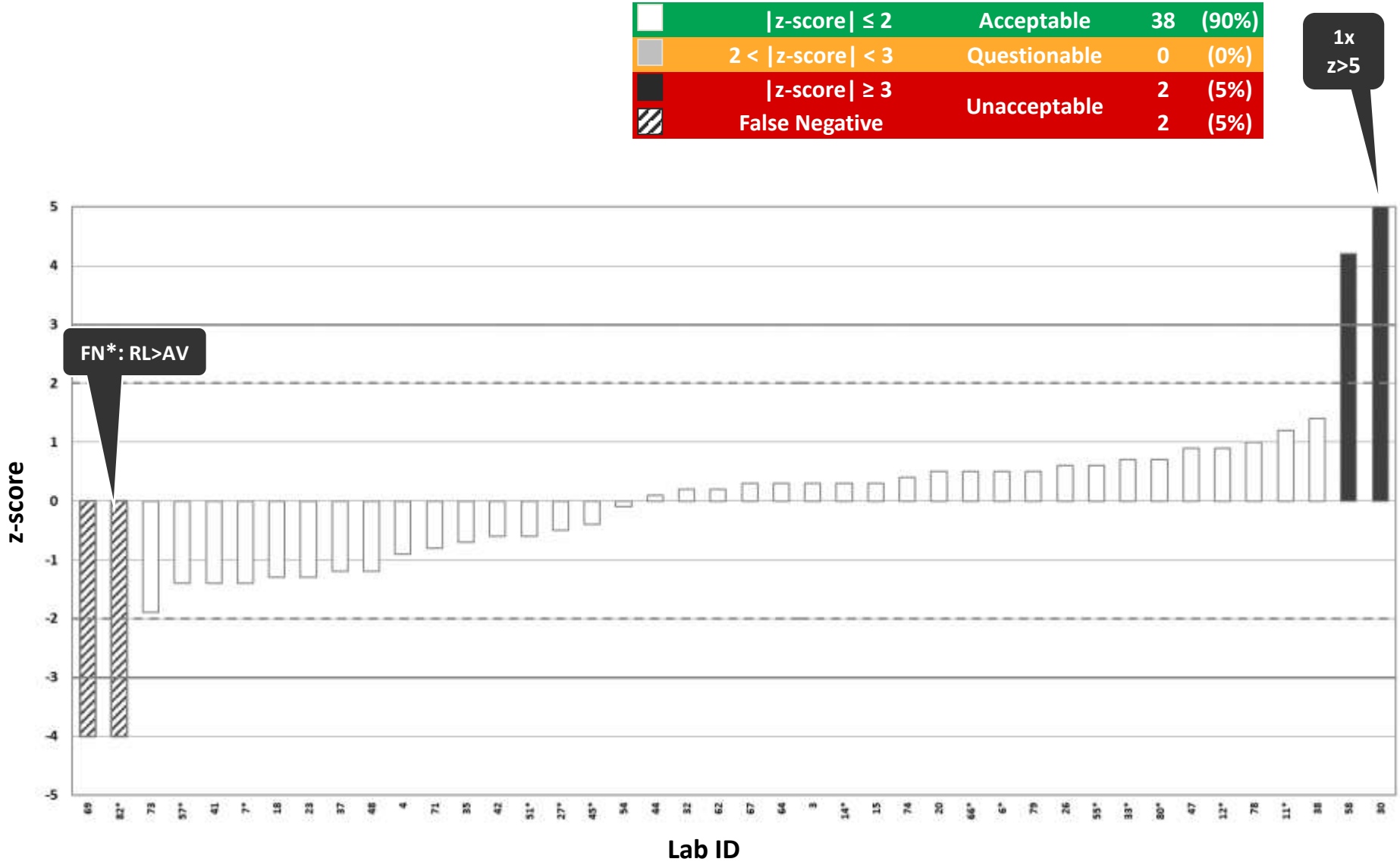
Results	39
False Neg.	1
AV	0.0873 [mg/kg]
CV*	16.9 %
MRRL	0.01 [mg/kg]
UAV-test	passed



Nicotine

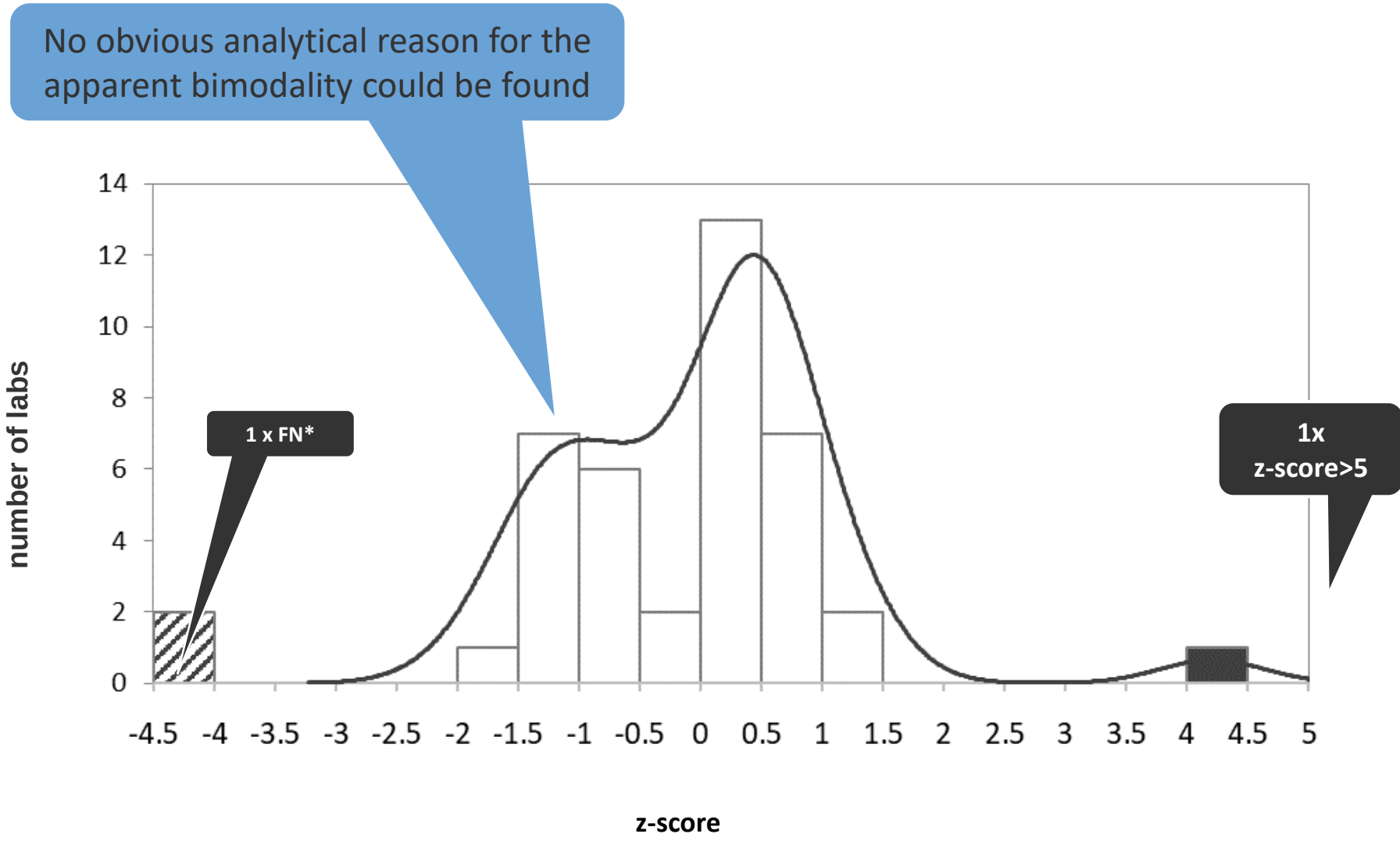
Results	40
False Neg.	1 + 1 (FN*)
AV	0.0877 [mg/kg]
CV*	25.3 %
MRRL	0.01 [mg/kg]
UAV-test	passed

	|z-score| ≤ 2	Acceptable	38	(90%)
	2 < |z-score| < 3	Questionable	0	(0%)
	|z-score| ≥ 3	Unacceptable	2	(5%)
	False Negative		2	(5%)



Nicotine

Results	40
False Neg.	1 + 1 (FN*)
AV	0.0877 [mg/kg]
CV*	25.3 %
MRRL	0.01 [mg/kg]
UAV-test	passed



Nicotine

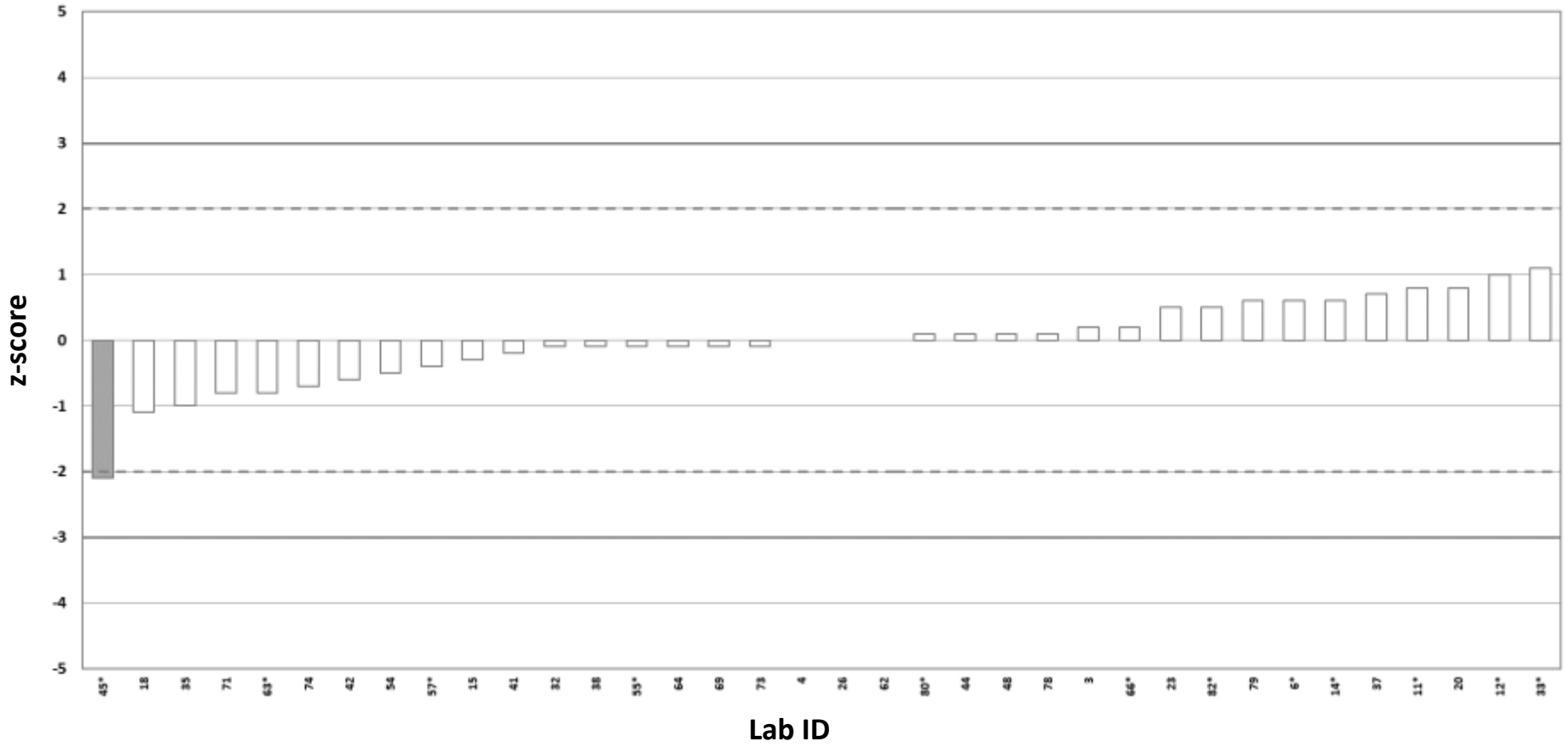
Impact of using ILIS

NICOTINE	Total	ILIS-Yes	ILIS-No
Values	42	12	30
Median	0,094	0,092	0,095
Robust Mean	0,088	0,085	0,090
CV*	26%	23%	28%
RSD	49%	21%	56%

Oxymatrine

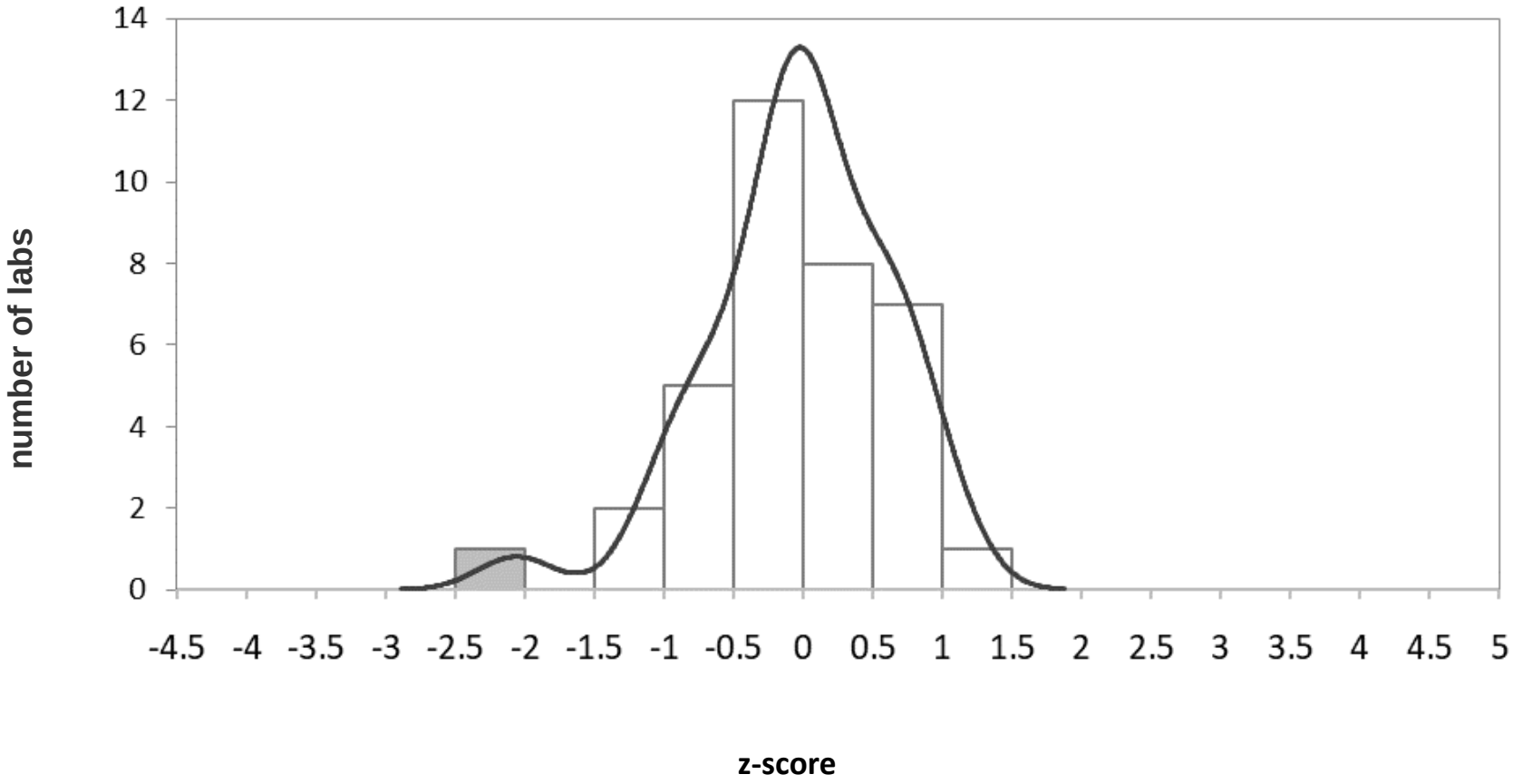
Results	36
False Neg.	0
AV	0.0681 [mg/kg]
CV*	15.4 %
MRRL	0.01 [mg/kg]
UAV-test	passed

	|z-score| ≤ 2	Acceptable	35	(97%)
	2 < |z-score| < 3	Questionable	1	(3%)
	|z-score| ≥ 3	Unacceptable	0	(0%)
	False Negative		0	(0%)



Oxymatrine

Results	36
False Neg.	0
AV	0.0681 [mg/kg]
CV*	15.4 %
MRRL	0.01 [mg/kg]
UAV-test	passed

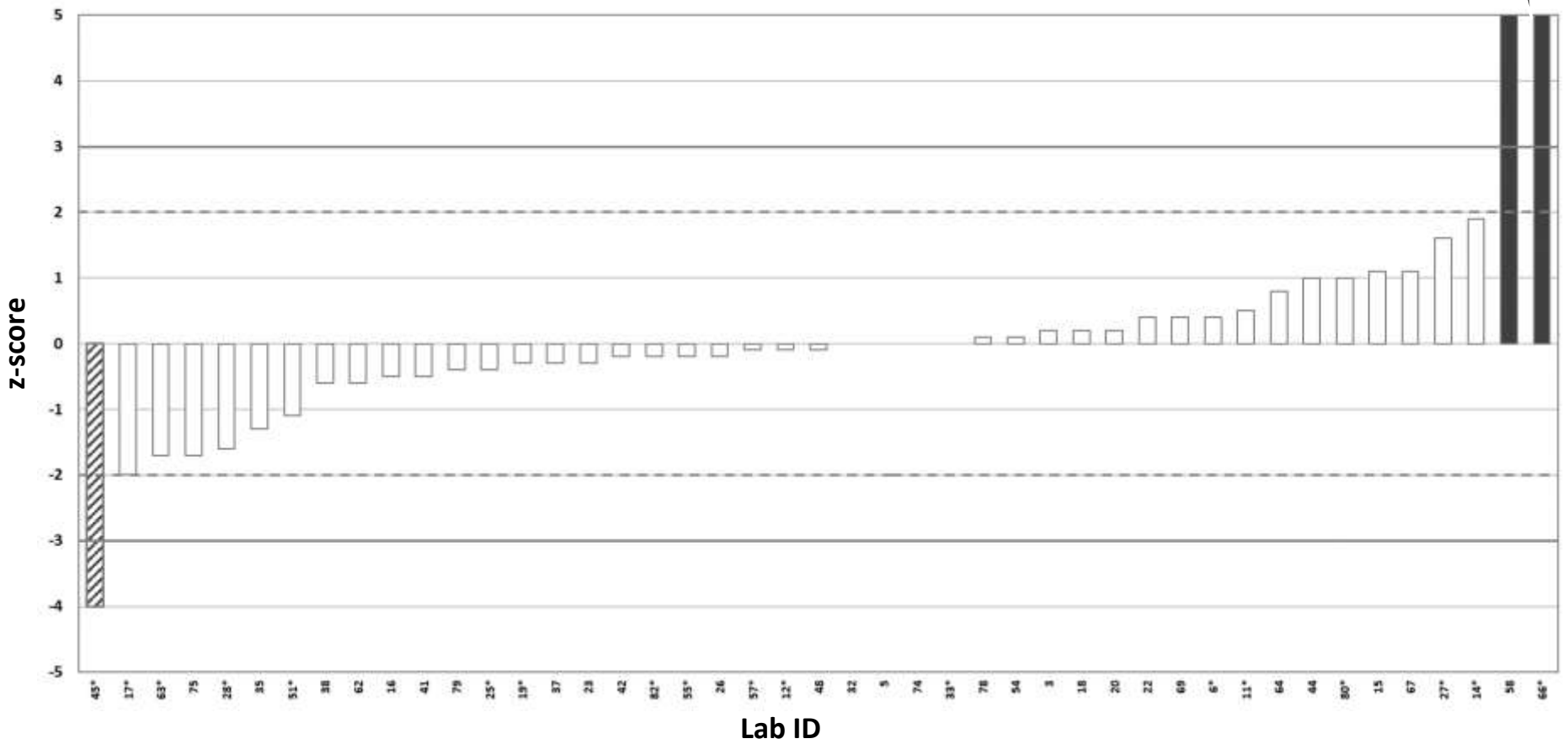


Phosphonic acid

Results	44
False Neg.	1
AV	0.202 [mg/kg]
CV*	20.9 %
MRRL	0.03 [mg/kg]
UAV-test	passed

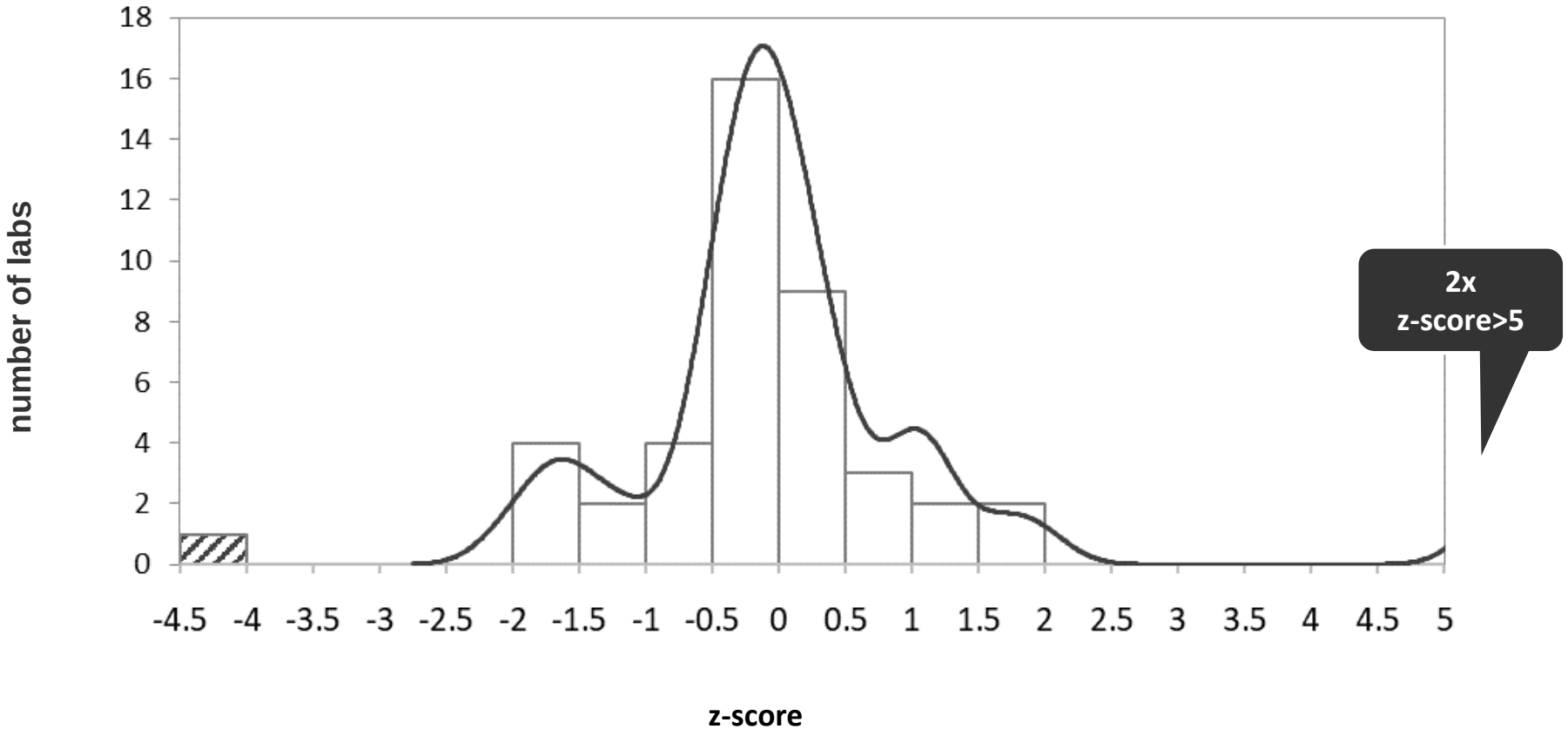
	|z-score| ≤ 2	Acceptable	42	(90%)
	2 < |z-score| < 3	Questionable	0	(0%)
	|z-score| ≥ 3	Unacceptable	2	(5%)
	False Negative		1	(5%)

2x z>5



Phosphonic acid

Results	44
False Neg.	1
AV	0.202 [mg/kg]
CV*	20.9 %
MRRL	0.03 [mg/kg]
UAV-test	passed



Phosphonic acid

Impact of using ILIS

PHOSPHONIC ACID	Total	ILIS-Yes	ILIS-No
Values	47	23	24
Median	0,197	0,199	0,196
Robust Mean	0,200	0,197	0,206
CV*	**21%**	**15%**	**30%**
RSD	**36%**	**18%**	**46%**

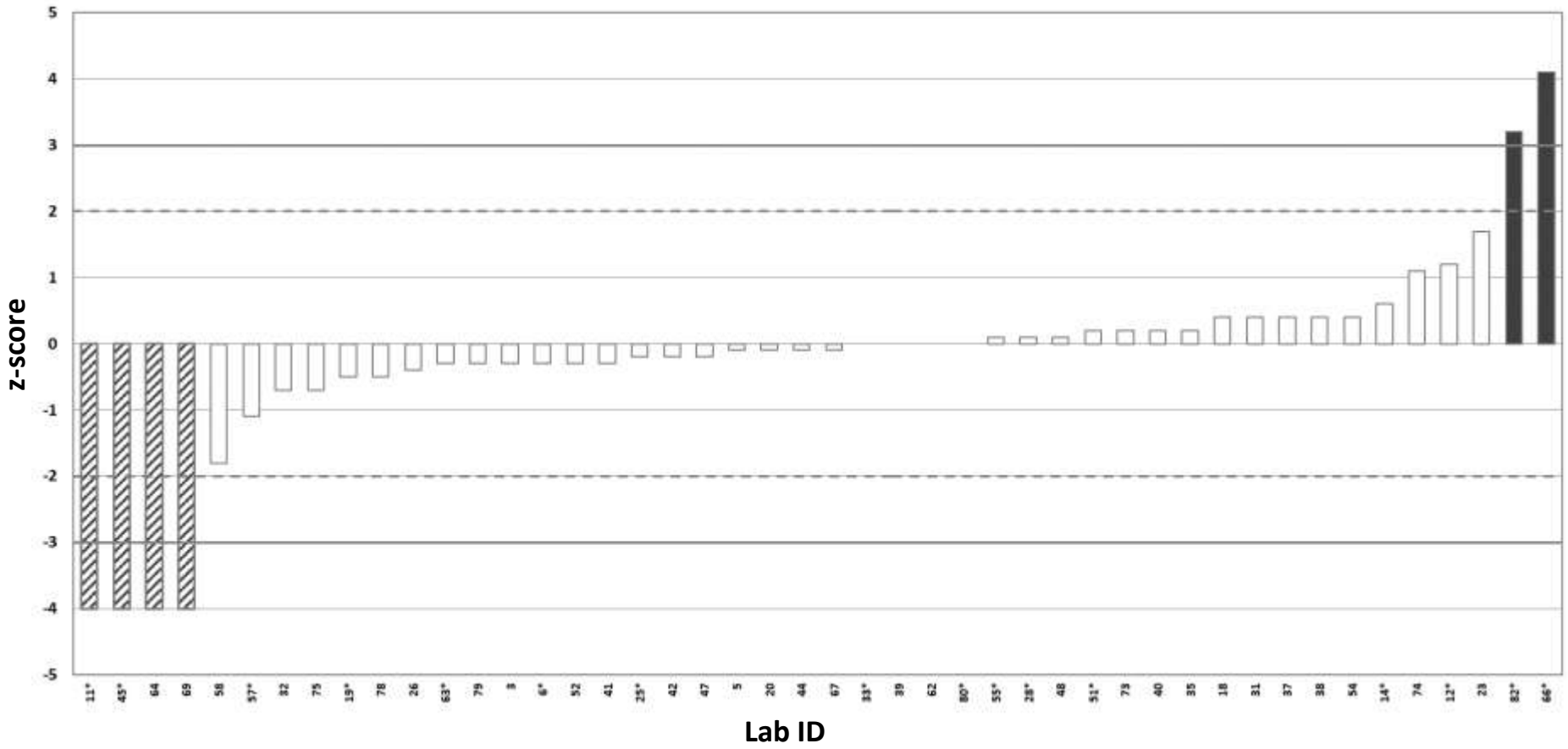
RESULT OVERVIEW

OPTIONAL Compounds

Perchlorate anion

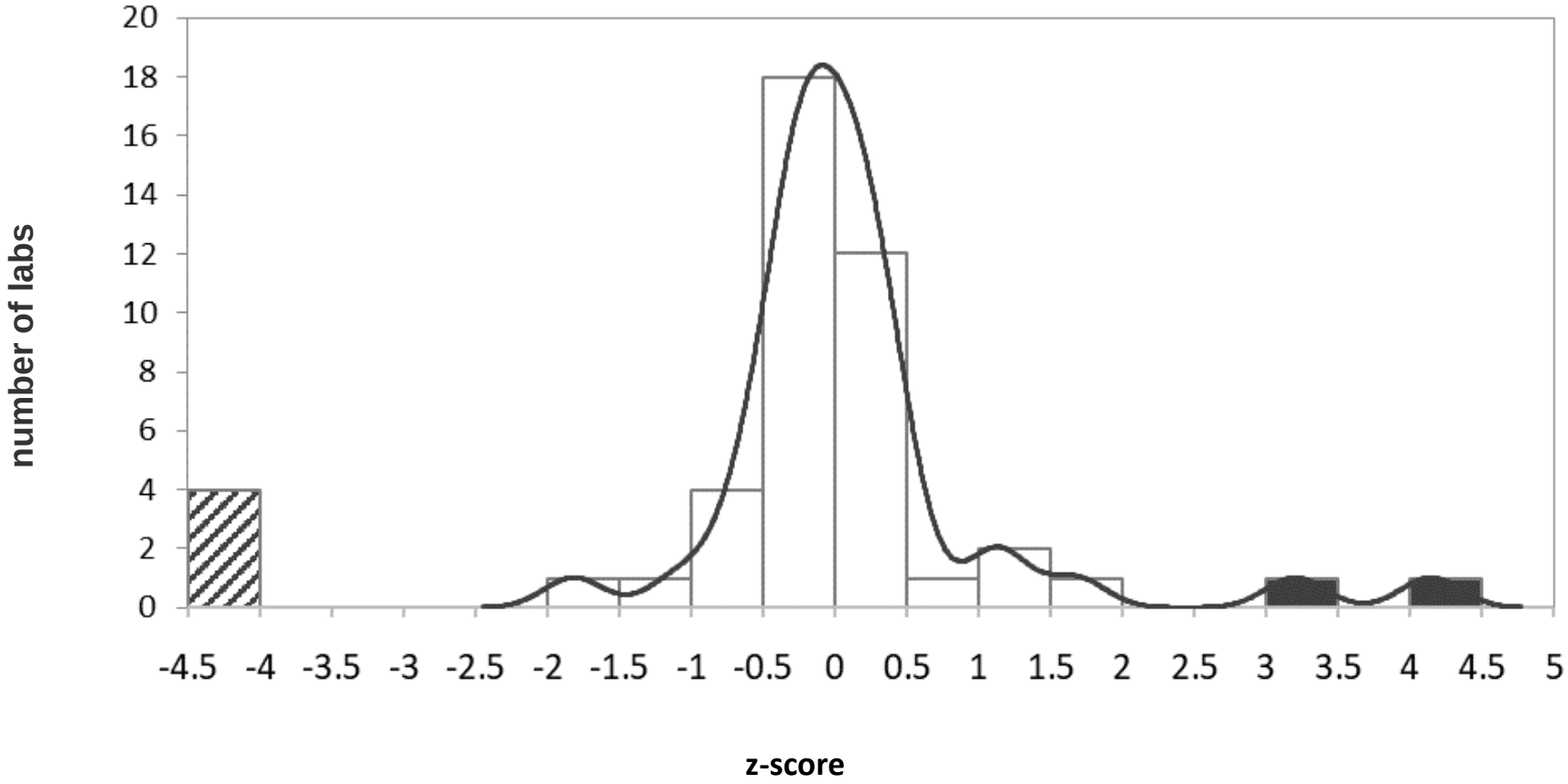
Results	42
False Neg.	4
AV	0.055 [mg/kg]
CV*	11.6 %
MRRL	0.01 [mg/kg]
UAV-test	passed

	|z-score| ≤ 2	Acceptable	40	(87%)
	2 < |z-score| < 3	Questionable	0	(0%)
	|z-score| ≥ 3	Unacceptable	2	(4%)
	False Negative		4	(9%)



Perchlorate (anion)

Results	42
False Neg.	4
AV	0.055 [mg/kg]
CV*	11.6 %
MRRL	0.01 [mg/kg]
UAV-test	passed



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Perchlorate anion

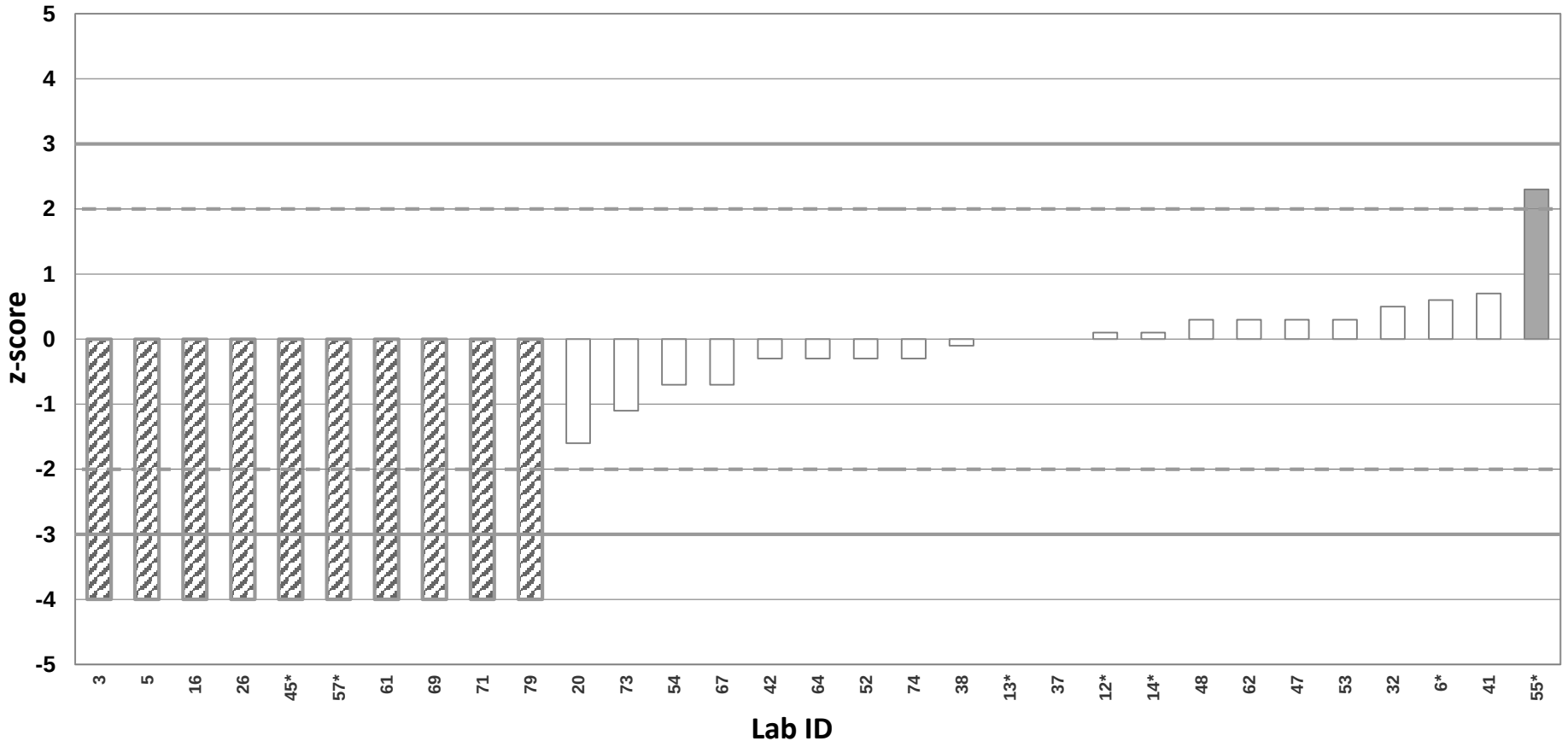
Impact of using ILIS

PERCHLORATE	Total	ILIS-Yes	ILIS-No
Values	44	28	16
Median	0,055	0,055	0,053
Robust Mean	0,055	0,055	0,054
CV*	**11%**	**8%**	**19%**
RSD	**24%**	**19%**	**34%**

Trinexapac free acid

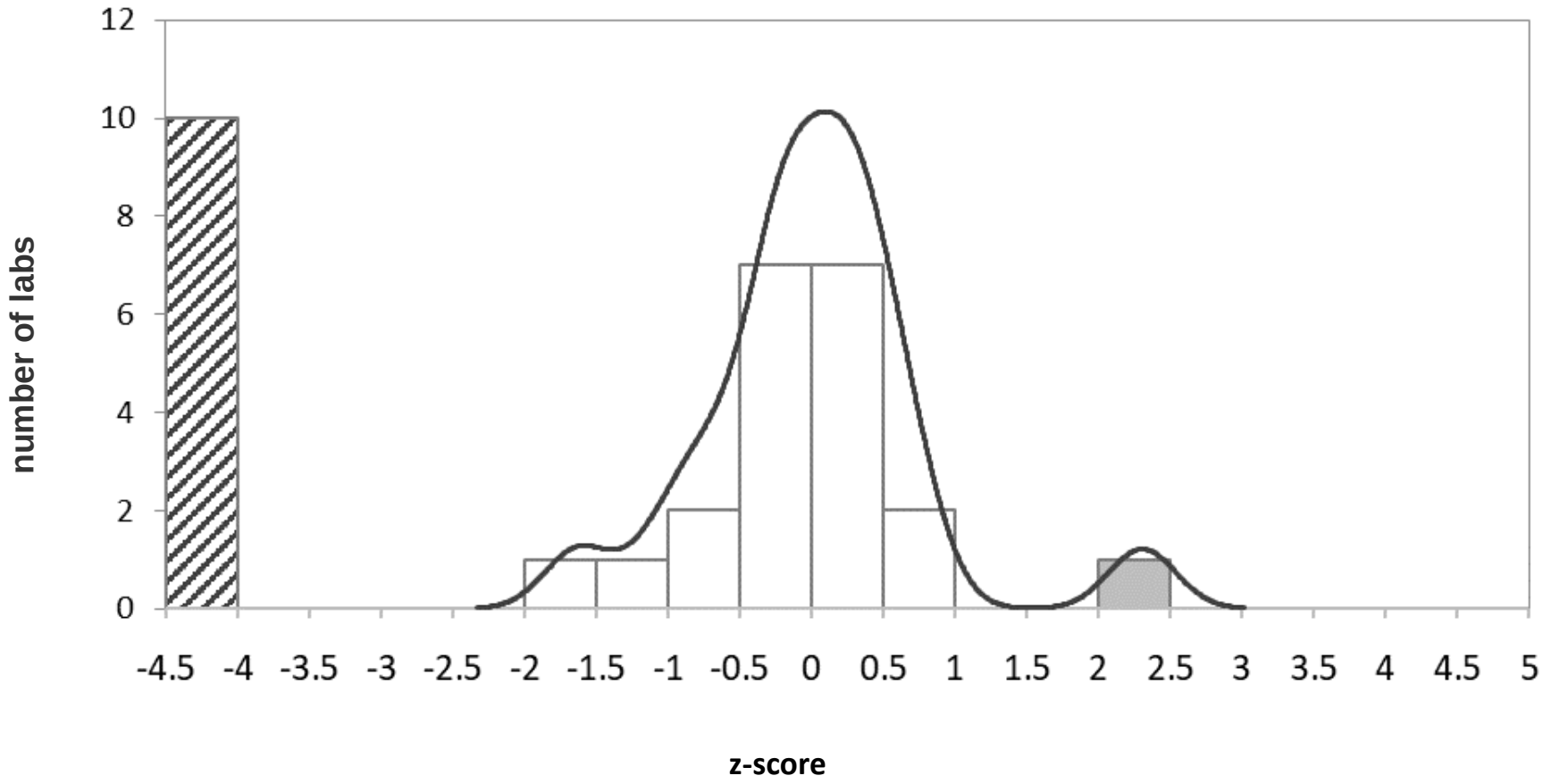
Results	21
False Neg.	10
AV	0.118 [mg/kg]
CV*	14.7 %
MRRL	0.01 [mg/kg]
UAV-test	passed

	|z-score| ≤ 2	Acceptable	20	(70%)
	2 < |z-score| < 3	Questionable	1	(0%)
	|z-score| ≥ 3	Unacceptable	0	(4%)
	False Negative		10	(33%)



Trinexapac free acid

Results	21
False Neg.	10
AV	0.118 [mg/kg]
CV*	14.7 %
MRRL	0.01 [mg/kg]
UAV-test	passed



Uncertainty of assigned value

COMPULSORY / OPTIONAL / Extra Compounds

EU+EFTA

Compound	No. of FNs | Outlier	No. of Numerical Results	AV [mg/kg]	CV* [%]	Uncertainty of AV (UAV) [mg/kg]	UAV-Tolerance [mg/kg]	Judgement
2,4-D (free acid)	0 | 0	60	0.052	18.9%	0.0016	0.0039	passed
BAC-C14 chloride	3 | 1	42	0.119	19.0%	0.0044	0.0089	passed
Chlorate (anion)	3 | 1	45	0.102	9.8%	0.0019	0.0077	passed
DDAC-C10 chloride	2 | 1	44	0.149	25.0%	0.0071	0.0112	passed
Fluazifop (free acid)	1 | 2	58	0.060	16.5%	0.0017	0.0045	passed
Glyphosate	1 | 4	63	0.102	12.8%	0.0021	0.0077	passed
Matrine	1 | 0	39	0.087	16.9%	0.0029	0.0065	passed
Nicotine	2 | 1	40	0.088	25.3%	0.0044	0.0066	passed
Oxymatrine	0 | 0	36	0.068	15.4%	0.0022	0.0051	passed
Phosphonic acid	1 | 2	44	0.202	20.9%	0.0082	0.0152	passed
Perchlorate	4 | 2	42	0.055	11.6%	0.0013	0.0041	passed
Trinexapac (free acid)	10 | 0	21	0.118	14.7%	0.0047	0.0089	passed
Compound	**No. of not detected | Outlier**	**No. of Numerical Results**	**AV [mg/kg]**	**CV* [%]**	**Uncertainty of AV (UAV) [mg/kg]**	**UAV-Tolerance [mg/kg]**	**Judgement**
Bromide ion	28 | ?	6	–	–	–	–	
Copper	2 | ?	10	–	–	–	–	

Overall Performance I

COMPULSORY / OPTIONAL / Extra Compounds

EU+EFTA

Compound	No. of Labs (all)	FNs (therein)	AAZ	CV* [%]
2,4-D (free acid)	60	0	0.6	18.9%
BAC-C14 chloride	45	3	1.0	19.0%
Chlorate (anion)	48	3	0.6	9.8%
DDAC-C10 chloride	46	2	1.0	25.0%
Fluazifop (free acid)	59	1	0.7	16.5%
Glyphosate	64	1	0.7	12.8%
Matrine	40	1	0.6	16.9%
Nicotine	42	2	1.1	24.8%
Oxymatrine	36	0	0.5	15.4%
Phosphonic acid	45	1	0.9	20.9%
Perchlorate	60	0	0.9	18.9%
Trinexapac (free acid)	31	10	1.6	14.7%
Bromide ion	34	28	1.1	–
Copper	12	2	1.5	–

Overall Performance II

Rules for Category A:

EU+EFTA

- Analysed for at least 13 out of 15 compulsory pesticides
- Correctly found at least 9 out of 10 compulsory pesticides present in test item
- No FPs among compulsory analytes

	No. of Labs	[%]
Category A	28	39 %
Category B	43	61 %

Methods used

Zeilenbeschriftungen	QuEChERS	MiniLuke	SweEt	Chemelut	Dil&Shoot-QuPPe-like	Dilute&Shoot-Other	Gly-Deriv	Br-Deriv	copper-various	noData	Gesamtergebnis	QuEChERS	QuPPe-Style	Derivatisation	QuEChERS	MiniLuke	SweEt	Chemelut	Dil&Shoot-QuPPe-like	Dilute&Shoot-Other	Gly-Deriv	Br-Deriv	copper-various
DDAC-C10 chloride	42	1	2		1	1				1	48	88%	4%		88%	2%	4%	0%	2%	2%	0%	0%	0%
BAC-C14 chloride	40	1	2		2	1				1	47	85%	6%		85%	2%	4%	0%	4%	2%	0%	0%	0%
2,4-D (free acid)	55	2	2	1	3						63	87%	5%		87%	3%	3%	2%	5%	0%	0%	0%	0%
Fluazifop (free acid)	54	2	2	1	3						62	87%	5%		87%	3%	3%	2%	5%	0%	0%	0%	0%
Trinexapac (free acid)	24		2	1	2					3	32	75%	6%		75%	0%	6%	3%	6%	0%	0%	0%	0%
Nicotine	19			1	23	1					44	43%	55%		43%	0%	0%	2%	52%	2%	0%	0%	0%
Matrine	16		1	1	24	1					43	37%	58%		37%	0%	2%	2%	56%	2%	0%	0%	0%
Oxymatrine	14			1	23	1					39	36%	62%		36%	0%	0%	3%	59%	3%	0%	0%	0%
Bromide (anion)					22	3		8		3	36	0%	69%	22%	0%	0%	0%	0%	61%	8%	0%	22%	0%
Glyphosate					55	4	9				68	0%	87%	13%	0%	0%	0%	0%	81%	6%	13%	0%	0%
Chlorate (anion)					47	1				2	50	0%	96%		0%	0%	0%	0%	94%	2%	0%	0%	0%
Perchlorate					46	1				1	48	0%	98%		0%	0%	0%	0%	96%	2%	0%	0%	0%
Phosphonic acid					47	1					48	0%	100%		0%	0%	0%	0%	98%	2%	0%	0%	0%
Copper									13	1	14	0%	0%		0%	0%	0%	0%	0%	0%	0%	0%	93%

Use of ILIS

Analytes	NO	YES Spiked at…					Total Results
		the beginning	Final Extract	intermediate step	SUM	%	
Glyphosate	20	42	4	2	48	71%	68
Perchlorate	19	26	3		29	60%	48
Chlorate (anion)	20	27	3		30	60%	50
Phosphonic acid	24	21	3		24	50%	48
Nicotine	31	13			13	30%	44
Matrine	34	9			9	21%	43
2,4-D (free acid)	56	7			7	11%	63
DDAC-C10 chloride	43	5			5	10%	48
Oxymatrine	35	4			4	10%	39
BAC-C14 chloride	45	2			2	4%	47
Fluazifop (free acid)	61	1			1	2%	62
Trinexapac (free acid)	32				0	0%	32

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Poor performance and Feedback

Poor performance

- **25 EU/EFTA OfLs, 49 cases**
  (therein 28 cases of FNs)

- **Additionally „FN“ for Extra Compounds (natural content)**

Bromide Ion	28 cases	No MRRL set
Copper	2 cases	No MRRL set

Feedback on Poor Performance

- **21 EU/EFTA OfLs gave feedback for poor performance in 42 cases**

No. cases	Reasons
13	*Lack of experience*
10	*Others/Miscellaneous (e.g. Column equilibration, 1 injection in screening)*
9	*Analytical procedure was appropriate but it was not properly performed (e.g. important component - e.g. water- not used, extraction time too short/long)*
5	*Misinterpretation / Misevaluation of measurement data /* ***Wrong target pesticide assumed***
5	*Inappropriate / erroneous calibration approach*
4	*Analytical procedure was inappropriate*
4	*Calculation error (e.g. use of wrong factor, to express residue as required in PT; to address dilutions etc.)*
4	*Deficient QC-measures that would have helped to recognize that method generates FNs, FPs or strongly biased results (e.g. no recovery test)*

Thank You for Your Attention

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