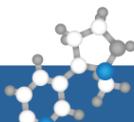


# **EUPT-SRM10**

# **Pesticide Residues in**

# **Corn Flour**

**M. Anastassiades**  
**P. Schreiter**  
**A. Barth**  
**D. Dörk**

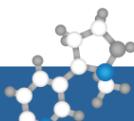


## COMMODITY SELECTION :

- **Maize** (selected during EUPT-AdvG meeting in 2013)

## PESTICIDE SELECTION (Considerations):

- a) SRM-Pesticides relevant for cereals and maize in particular
- b) Pesticides included in MACP Regulation or MACP Working Document:
  - MACP: Chlormequat, DTCs, Ethephon, Fenbutatin Oxide, Glyphosate, Mepiquat, Propamocarb.
  - MACP Working Document: 2,4-D, MCPA, Glufosinate (+metabolites), Ioxynil, Paraquat, Phosphonic acid, Flonicamid degradation products (TFNA, TFNG)
- c) Overall Capability of Labs
  - As known from previous EUPTs and pesticide scope
- d) Opinion of the EUPT-Scientific Committee
  - Selection of Pesticides in the **Target Pesticide List**
- e) Opinion of the EUPT-QC-Group
  - Selection of **pesticides to be spiked and approx. levels**



## Registration for EUPT-SRM10:

**25 March - 17 April 2015**

## Sample Shipment:

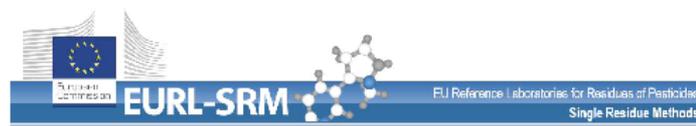
**18 May, 2015**

## Results Submission:

**26 May – 19 June, 2015**

## Preliminary Report:

**30 June, 2015**



### CALENDAR for the EUPT – SRM10

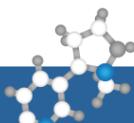
Maize flour

(update: 23 March, 2015)

| Activity                                                                                                                                                    | Who ?                                                                                                                              | Dates                  |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------|------------------------|
| Opening of the EUPT-SRM10 Website<br>with links to all relevant documents<br>(List of obliged labs, Calendar, Target Pesticides List, General Protocol)     | EURL-SRM                                                                                                                           | Jan. – Feb. 2015       |
| Registration via "EUPT-Registration Website"<br>(Note: obliged OFTs MUST enter this Website and either register or give explanations for non-participation) | - Obligated OFTs from EU-MSS<br>- OFTs from EFTA Countries<br>- OFTs from EU-candidate C.<br>- Labs from 3 <sup>rd</sup> Countries | 25 Mar. - 17 Apr. 2015 |
| Dispatch of EUPT-SRM10-Specific Protocol                                                                                                                    | EURL-SRM                                                                                                                           | Apr. 2015              |
| Preparation of EUPT-SRM10-Test item<br>(preliminary tests Spiking / Homogenization)                                                                         | EURL-SRM                                                                                                                           | Jan. – May 2015        |
| Homogeneity Tests                                                                                                                                           | EURL-SRM                                                                                                                           | May 2015               |
| Stability Tests                                                                                                                                             | EURL-SRM                                                                                                                           | May – June 2015        |
| Shipment of EUPT-SRM10 Test Item<br>(Reminder of upcoming parcel arrival)                                                                                   | EURL-SRM                                                                                                                           | 18 May 2015            |
| Confirmation of sample Receipt and acceptance via<br>"EUPT-SRM10 Result Submission Website",<br>(Sub-Page 0)                                                | Participating Labs                                                                                                                 | within 48 h of receipt |
| Result Submission<br>(Pesticide scope, Results, Method Info) in<br>"EUPT-SRM10 Result Submission Website",<br>(Sub-Pages 1 – 3)                             | Participating Labs                                                                                                                 | 26 May – 19 June       |
| Preliminary Report<br>(only completion of results)                                                                                                          | EURL-SRM                                                                                                                           | July 2015              |
| EUPT Evaluation Meeting                                                                                                                                     | EUPT-SC, DG-SANCO                                                                                                                  | July 2015              |
| Survey to collect reasons for underperformance<br>and missing information on methods                                                                        | EURL-SRM / Participating Labs                                                                                                      | July 2015              |
| Final Report                                                                                                                                                | EURL-SRM                                                                                                                           | Dec. 2015              |

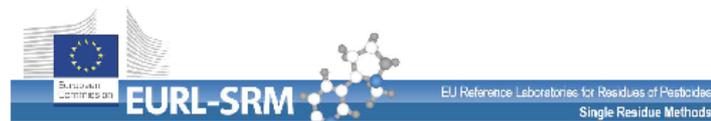
**REMARK:** Please note that the dates mentioned above may be subject to minor changes. In the case of changes the participants will be informed via e-mail. But still please check periodically our website for possible updates in case the email does not get through to you.  
contact: [eurl-srm@cvuas.bwl.de](mailto:eurl-srm@cvuas.bwl.de)

The EUPT-SRM Team



|            | In Target List | Present in Test Item      |                   |     |
|------------|----------------|---------------------------|-------------------|-----|
|            |                | Incurring (field treated) | Spiked in the lab | Sum |
| Compulsory | 9              | 2                         | 6                 | 8   |
| Optional*  | 14             |                           | 5                 | 5   |
| SUM        | 23             | 2                         | 11                | 13  |

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



TARGET PESTICIDE LIST  
for the EUPT – SRM10 2015  
Maize Flour  
last update on 03.03.2015

| Compounds Potentially Present in Test Item                                                                     | In MACP   | MRRL (mg/kg) |
|----------------------------------------------------------------------------------------------------------------|-----------|--------------|
| <b>Compulsory Compounds (will be considered in Category A/B classification)</b>                                |           |              |
| 2,4-D (free acid*)                                                                                             | MACP-WD   | 0.01         |
| Chlormequat (cation)                                                                                           | MACP-Reg. | 0.01         |
| Dithiocarbamates (including maneb, mancozeb, metiram, propineb, thiram and ziram) expressed as CS <sub>2</sub> | MACP-Reg. | 0.05         |
| Ethephon                                                                                                       | MACP-Reg. | 0.02         |
| Fenbutatin Oxide                                                                                               | MACP-Reg. | 0.02         |
| Glyphosate                                                                                                     | MACP-Reg. | 0.05         |
| MCPA (free acid*)                                                                                              | MACP-WD   | 0.01         |
| Mepiquat (cation)                                                                                              | MACP-Reg. | 0.01         |
| Propamocarb                                                                                                    | MACP-Reg. | 0.01         |
| <b>Optional Compounds (will NOT be considered in Category A/B classification)</b>                              |           |              |
| Bentazone (parent*)                                                                                            |           | 0.01         |
| Bromoxynil (free phenol*)                                                                                      |           | 0.01         |
| Dicamba (free acid*)                                                                                           |           | 0.02         |
| Dichlorprop (2,4-DP) including Dichlorprop-P (free acid*)                                                      |           | 0.01         |
| Fluroxypyr (free acid*)                                                                                        |           | 0.01         |
| Glufosinate (parent)                                                                                           | MACP-WD   | 0.02         |
| - N-Acetyl Glufosinate                                                                                         | MACP-WD   | 0.02         |
| - MPP (3-(hydroxymethylphosphinyl)propionic acid)                                                              | MACP-WD   | 0.02         |
| Isoxynil (free phenol*)                                                                                        | MACP-WD   | 0.01         |
| Mecoprop (MCP) including Mecoprop-P (free acid*)                                                               |           | 0.01         |
| Paraquat (dication)                                                                                            | MACP-WD   | 0.05         |
| Phosphonic acid (metabolite of Fosetyl)                                                                        | MACP-WD   | 0.05         |
| TFNA (metabolite of flonicamid)                                                                                | MACP-WD   | 0.02         |
| TFNG (metabolite of flonicamid)                                                                                | MACP-WD   | 0.02         |

Compulsory  
Optional

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](mailto:eurl-srm@cvuas.bwl.de)

The EUPT-SRM10 Organising Team

# PREPARATION OF TEST ITEM

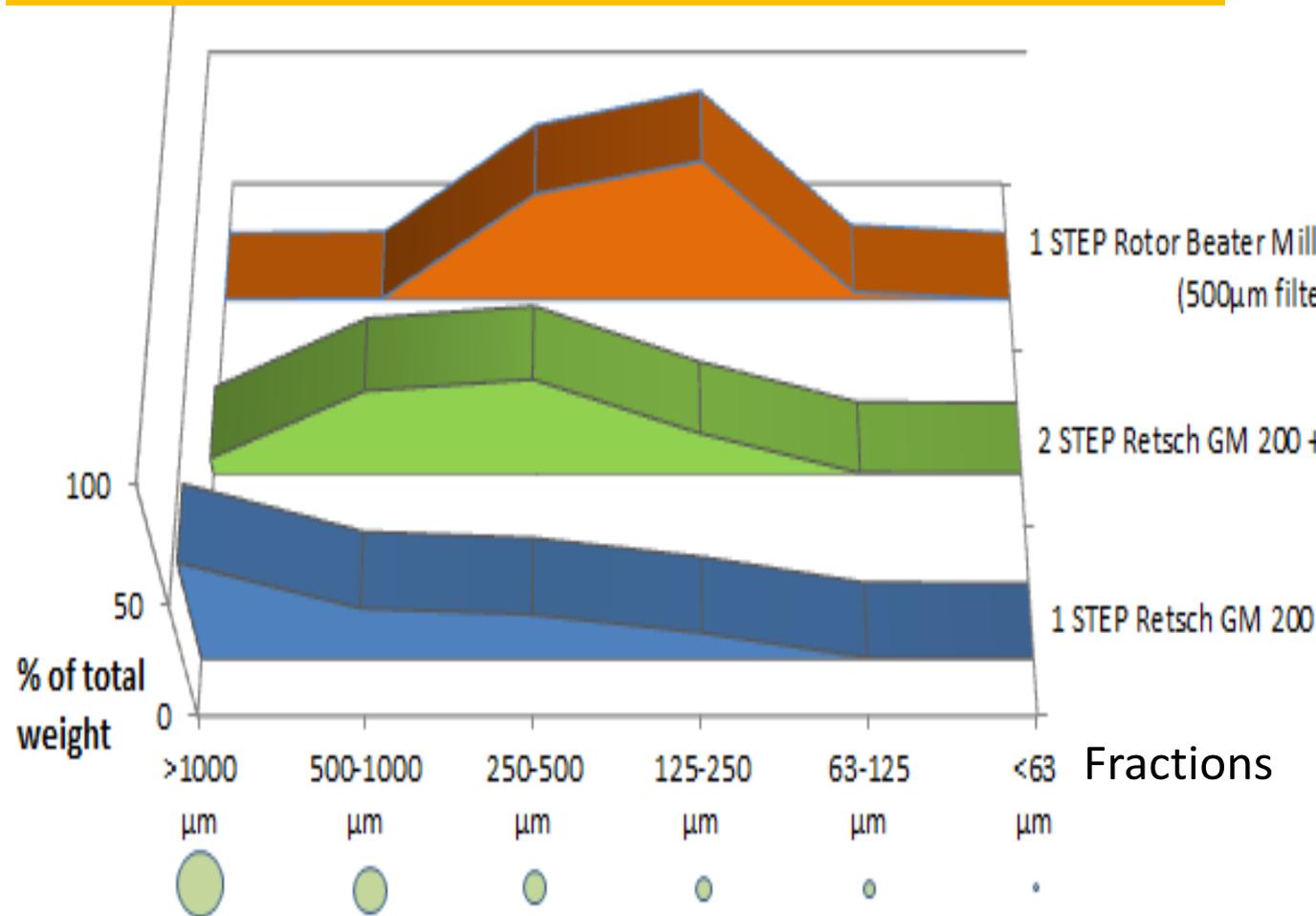


Ratio: ca. 3:1



# Maize with incurred Glyphosate milled in different ways

## Fractionation by particle size using sieves



1 STEP Rotor Beater Mill Retsch SR 300  
(500µm filter)

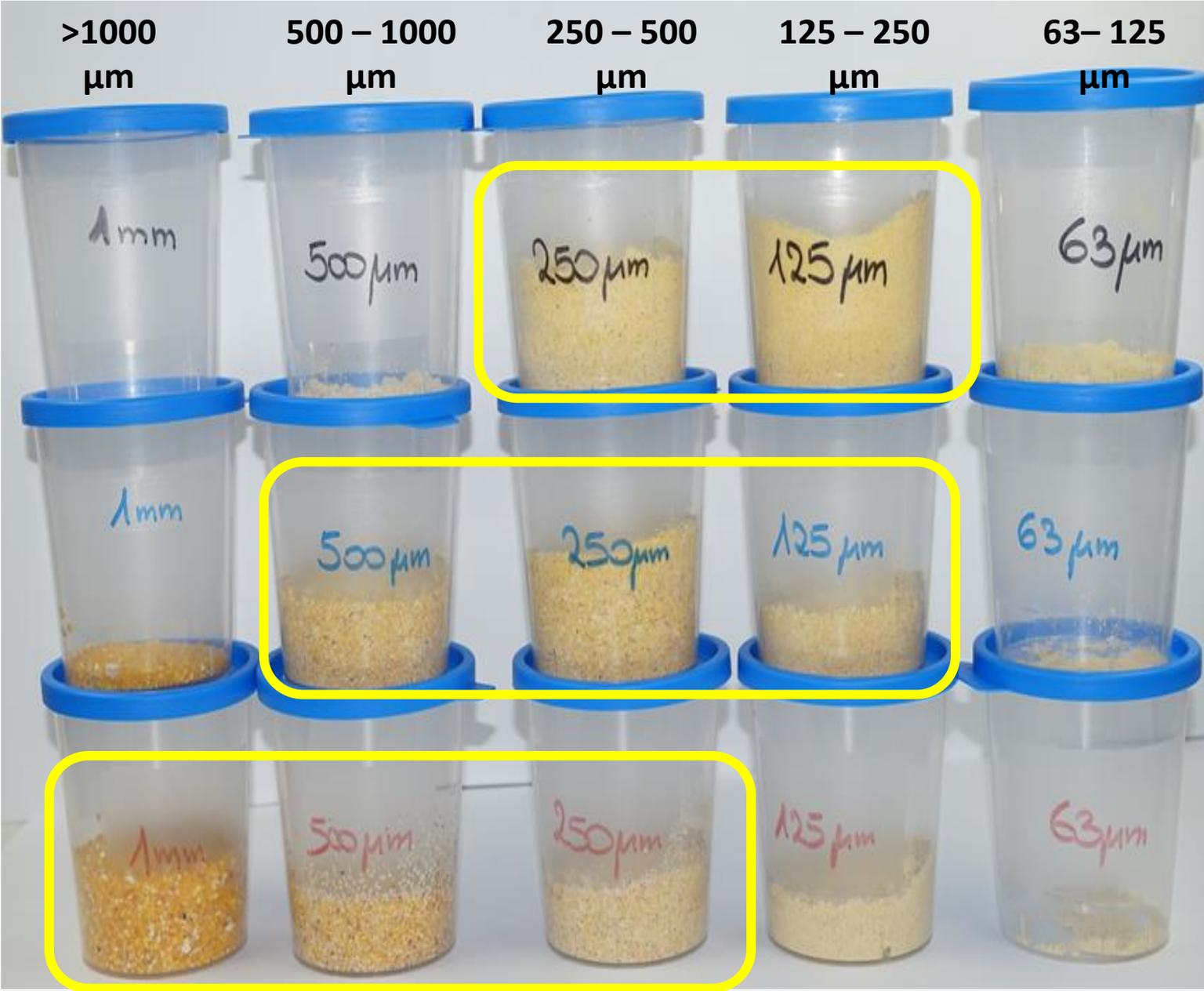
2 STEP Retsch GM 200 + IKA M20

1 STEP Retsch GM 200

Fractions



# Impact of milling on extractability



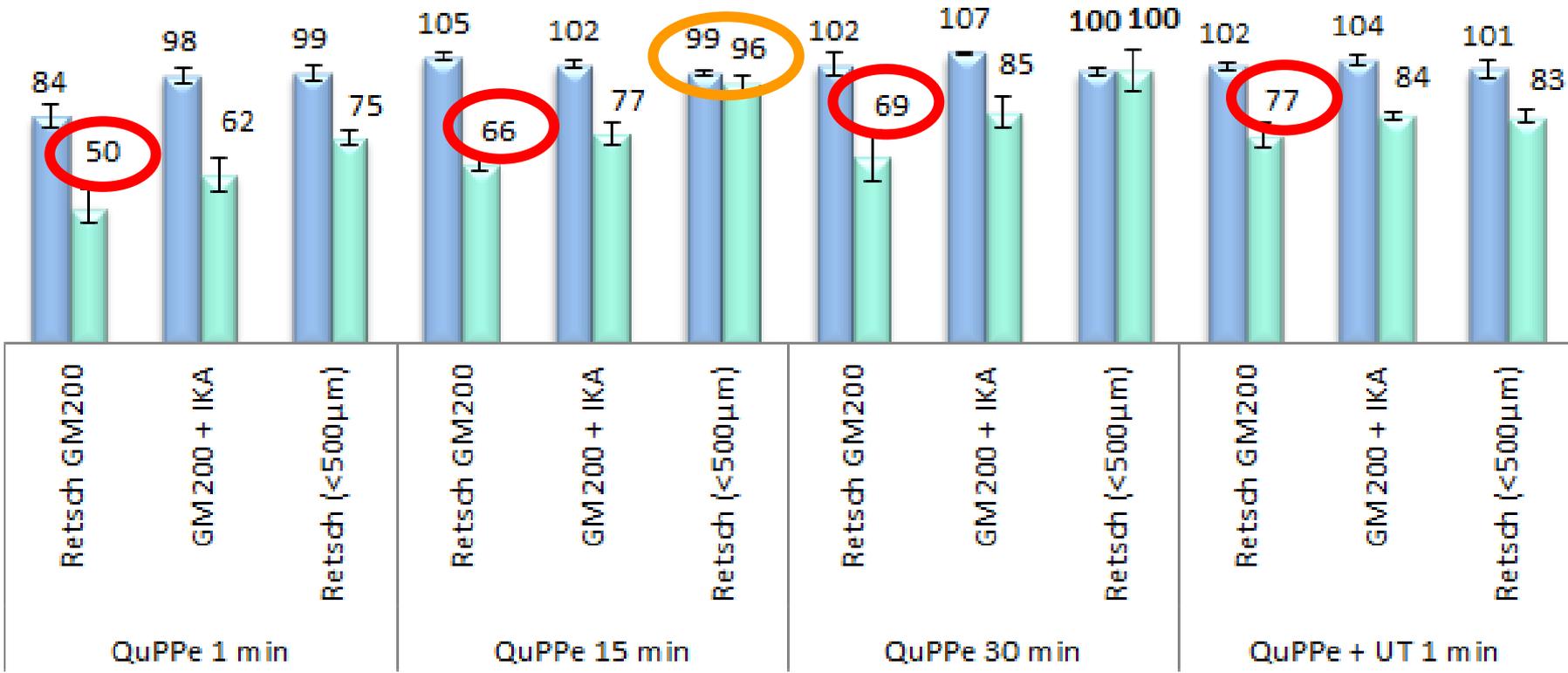
# Impact of milling on extractability

Maize with incurred Glyphosate and Chlormequat

### Concentration Chlormequat & Glyphosate, normalized [%]

Chlormequat    Glyphosate

set to 100 %



Pending Experiments: Milling at <200 μm, Impact of static wetting,

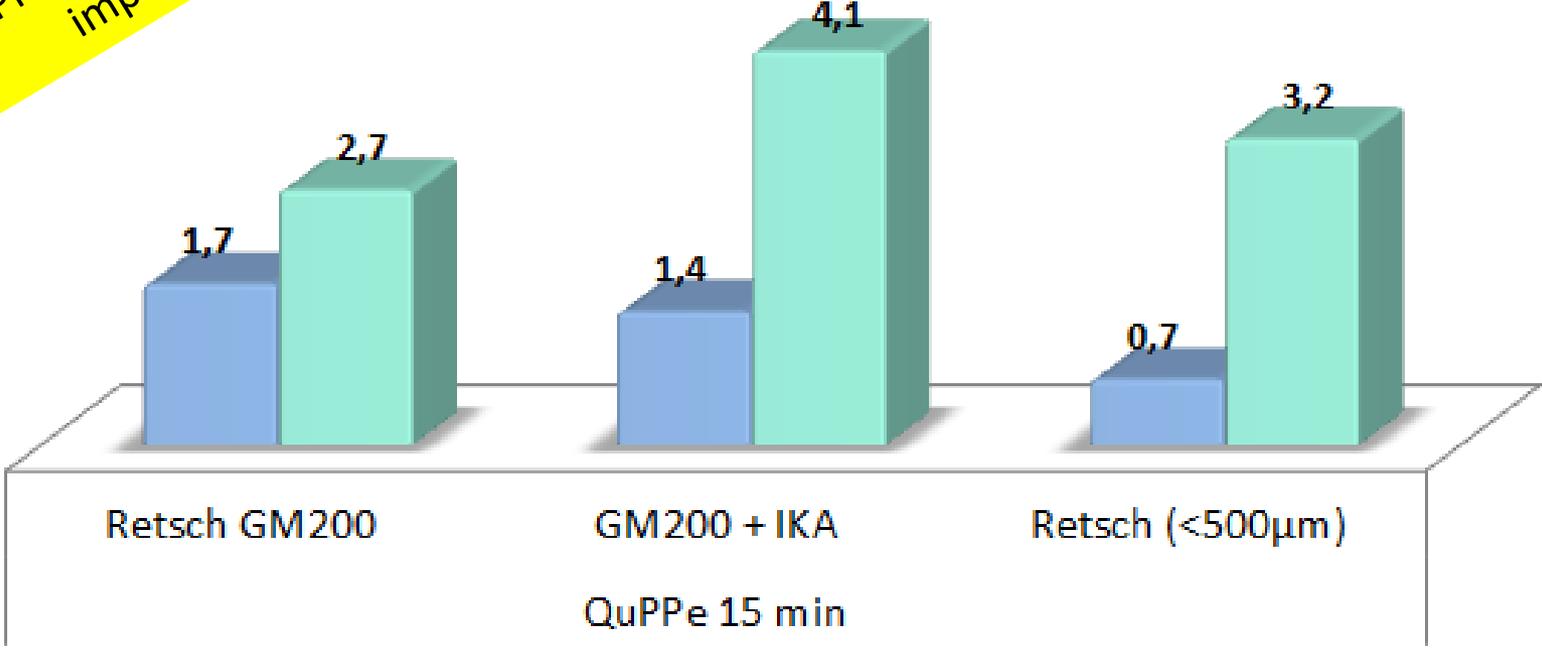
# Impact of milling on sub-sampling variability

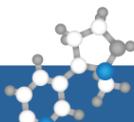
Maize with incurred Glyphosate and Chlormequat

### RSD Chlormequat & Glyphosate [%]

■ Chlormequat   ■ Glyphosate

Practically no impact





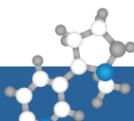
# HOMOGENEITY + STABILITY TEST (OVERVIEW)

## Compulsory Compounds:

| Compound    | Homog. Test | Stability Test |
|-------------|-------------|----------------|
| 2,4-D       | passed      | pending        |
| Chlormequat | passed      | pending        |
| Dithios     | passed      | pending        |
| Ethephon    | passed      | pending        |
| Glyphosate  | passed      | pending        |
| MCPA        | passed      | pending        |
| Mepiquat    | passed      | pending        |
| Propamocarb | passed      | pending        |

## Optional Compounds:

| Compound             | Homog. Test | Stability Test |
|----------------------|-------------|----------------|
| Bentazone            | passed      | pending        |
| Bromoxynil           | passed      | pending        |
| N-Acetyl Glufosinate | passed      | pending        |
| Phosphonic acid      | passed      | pending        |
| TFNG                 | passed      | pending        |



## COMPULSORY Compounds

|             | 2,4-D                 | Chlor-mequat          | Dithio-carbamates     | Ethephon              | Glyphosat             | MCPA                  | Mepiquat              | Propamocarb           |
|-------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| sample      | Concentration [mg/kg] |                       |                       |                       |                       |                       |                       |                       |
| 012         | 0.101 / 0.101         | 0.142 / 0.138         | 0.877 / 0.693         | 0.158 / 0.180         | 0.540 / 0.542         | 0.095 / 0.097         | 0.103 / 0.099         | 0.078 / 0.073         |
| 021         | 0.099 / 0.099         | 0.149 / 0.145         | 0.672 / 0.761         | 0.162 / 0.164         | 0.559 / 0.627         | 0.098 / 0.088         | 0.107 / 0.105         | 0.072 / 0.073         |
| 047         | 0.102 / 0.101         | 0.144 / 0.146         | 0.686 / 0.748         | 0.151 / 0.156         | 0.585 / 0.560         | 0.096 / 0.086         | 0.105 / 0.103         | 0.070 / 0.072         |
| 062         | 0.098 / 0.100         | 0.145 / 0.142         | 0.778 / 0.748         | 0.167 / 0.162         | 0.604 / 0.549         | 0.094 / 0.087         | 0.108 / 0.109         | 0.074 / 0.071         |
| 083         | 0.101 / 0.100         | 0.142 / 0.145         | 0.948 / 0.813         | 0.163 / 0.161         | 0.603 / 0.583         | 0.099 / 0.082         | 0.099 / 0.096         | 0.075 / 0.070         |
| 093         | 0.102 / 0.099         | 0.147 / 0.140         | 0.773 / 0.834         | 0.161 / 0.168         | 0.590 / 0.551         | 0.094 / 0.088         | 0.104 / 0.098         | 0.076 / 0.072         |
| 098         | 0.092 / 0.095         | 0.146 / 0.146         | 0.755 / 0.831         | 0.159 / 0.154         | 0.554 / 0.603         | 0.088 / 0.092         | 0.103 / 0.102         | 0.071 / 0.074         |
| 115         | 0.103 / 0.097         | 0.145 / 0.146         | 0.671 / 0.801         | 0.156 / 0.165         | 0.581 / 0.534         | 0.090 / 0.084         | 0.100 / 0.105         | 0.074 / 0.074         |
| 133         | 0.100 / 0.101         | 0.143 / 0.136         | 0.925 / 0.782         | 0.162 / 0.147         | 0.566 / 0.609         | 0.089 / 0.088         | 0.098 / 0.106         | 0.070 / 0.073         |
| 152         | 0.093 / 0.091         | 0.140 / 0.140         | 0.900 / 0.639         | 0.165 / 0.166         | 0.607 / 0.566         | 0.092 / 0.088         | 0.101 / 0.102         | 0.074 / 0.074         |
| mean        | 0.099                 | 0.143                 | 0.782                 | 0.161                 | 0.575                 | 0.091                 | 0.103                 | 0.073                 |
| $S_{sam}^2$ | $5.49 \times 10^{-5}$ | $1.16 \times 10^{-4}$ | $3.44 \times 10^{-3}$ | $1.46 \times 10^{-4}$ | $1.86 \times 10^{-3}$ | $4.62 \times 10^{-5}$ | $5.93 \times 10^{-5}$ | $3.01 \times 10^{-5}$ |
| $c$         | $1.06 \times 10^{-4}$ | $2.25 \times 10^{-4}$ | $1.55 \times 10^{-2}$ | $3.20 \times 10^{-4}$ | $4.43 \times 10^{-3}$ | $1.19 \times 10^{-4}$ | $1.20 \times 10^{-4}$ | $6.18 \times 10^{-5}$ |
|             | passed                |

## OPTIONAL Compounds

|                 | Bentazone                    | Bromoxynil            | N-Acetyl Glufosinate  | Phosphonic acid       | TFNG                  |
|-----------------|------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| sample          | <b>Concentration [mg/kg]</b> |                       |                       |                       |                       |
| <b>012</b>      | 0.113 / 0.104                | 0.136 / 0.125         | 0.175 / 0.192         | 0.666 / 0.716         | 0.176 / 0.176         |
| <b>021</b>      | 0.099 / 0.100                | 0.123 / 0.123         | 0.185 / 0.184         | 0.636 / 0.706         | 0.162 / 0.153         |
| <b>047</b>      | 0.115 / 0.113                | 0.138 / 0.138         | 0.183 / 0.184         | 0.701 / 0.644         | 0.178 / 0.174         |
| <b>062</b>      | 0.102 / 0.106                | 0.125 / 0.133         | 0.177 / 0.198         | 0.671 / 0.724         | 0.163 / 0.173         |
| <b>083</b>      | 0.103 / 0.106                | 0.127 / 0.134         | 0.200 / 0.162         | 0.691 / 0.695         | 0.162 / 0.176         |
| <b>093</b>      | 0.108 / 0.100                | 0.136 / 0.126         | 0.186 / 0.195         | 0.674 / 0.665         | 0.171 / 0.154         |
| <b>098</b>      | 0.104 / 0.104                | 0.127 / 0.127         | 0.181 / 0.191         | 0.702 / 0.772         | 0.159 / 0.164         |
| <b>115</b>      | 0.101 / 0.100                | 0.125 / 0.129         | 0.167 / 0.186         | 0.766 / 0.660         | 0.166 / 0.161         |
| <b>133</b>      | 0.101 / 0.105                | 0.130 / 0.127         | 0.178 / 0.204         | 0.729 / 0.640         | 0.168 / 0.173         |
| <b>152</b>      | 0.097 / 0.105                | 0.125 / 0.127         | 0.198 / 0.190         | 0.711 / 0.737         | 0.174 / 0.169         |
| <b>mean</b>     | <b>0.104</b>                 | <b>0.129</b>          | <b>0.186</b>          | <b>0.695</b>          | <b>0.168</b>          |
| $S_{sam}^2$     | $6.13 \times 10^{-5}$        | $9.38 \times 10^{-5}$ | $1.94 \times 10^{-4}$ | $2.72 \times 10^{-3}$ | $1.58 \times 10^{-4}$ |
| $c$             | $1.28 \times 10^{-4}$        | $1.94 \times 10^{-4}$ | $5.42 \times 10^{-4}$ | $7.06 \times 10^{-3}$ | $3.38 \times 10^{-4}$ |
| $S_{sam}^2 < C$ | <b>passed</b>                | <b>passed</b>         | <b>passed</b>         | <b>passed</b>         | <b>passed</b>         |

## COMPULSORY Compounds

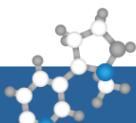
| Sample                                           | 2,4-D<br>[mg/kg] |              |              | Chlormequat<br>[mg/kg] |              |              | Dithiocarbamates<br>[mg/kg] |              |              | Ethephon<br>[mg/kg] |              |              |
|--------------------------------------------------|------------------|--------------|--------------|------------------------|--------------|--------------|-----------------------------|--------------|--------------|---------------------|--------------|--------------|
|                                                  | 08 May           | 16 June      | 07 July      | 07 May                 | 16 June      | 07 July      | 24 June                     | 08 Aug       | 08 Sept      | 07 May              | 16 June      | 07 July      |
| 47                                               | 0,097            | 0,100        | 0,106        | 0,139                  | 0,133        | 0,147        | 0,717                       | 0,776        | 0,783        | 0,178               | 0,165        | 0,170        |
| 93                                               | 0,099            | 0,100        | 0,103        | 0,138                  | 0,145        | 0,148        | 0,804                       | 0,761        | 0,779        | 0,176               | 0,165        | 0,175        |
| 152                                              | 0,096            | 0,098        | 0,098        | 0,147                  | 0,138        | 0,135        | 0,770                       | 0,804        | 0,782        | 0,173               | 0,159        | 0,174        |
| <b>Mean</b>                                      | <b>0,097</b>     | <b>0,099</b> | <b>0,102</b> | <b>0,141</b>           | <b>0,139</b> | <b>0,144</b> | <b>0,763</b>                | <b>0,780</b> | <b>0,782</b> | <b>0,176</b>        | <b>0,163</b> | <b>0,173</b> |
| % Difference<br>(vs. 1 <sup>st</sup> . analysis) | —                | 2,22 %       | 5,07 %       | —                      | -1,71 %      | 1,66 %       | —                           | 2,25 %       | 2,40 %       | —                   | -7,16 %      | -1,66 %      |
| Diff (mean)                                      |                  | 0,002        | 0,005        |                        | 0,002        | 0,002        |                             | 0,017        | 0,018        |                     | 0,013        | 0,003        |
| 0,3* FFP-SD                                      |                  | 0,007        | 0,007        |                        | 0,011        | 0,011        |                             | 0,057        | 0,057        |                     | 0,013        | 0,013        |
| Judgement                                        |                  | passed       | passed       |                        | passed       | passed       |                             | passed       | passed       |                     | passed       | passed       |

| Sample                                           | Glyphosate<br>[mg/kg] |              |              | MCPA<br>[mg/kg] |              |              | Mepiquat<br>[mg/kg] |              |              | Propamocarb<br>[mg/kg] |              |              |
|--------------------------------------------------|-----------------------|--------------|--------------|-----------------|--------------|--------------|---------------------|--------------|--------------|------------------------|--------------|--------------|
|                                                  | 07 May                | 16 June      | 07 July      | 08 May          | 16 June      | 07 July      | 07 May              | 16 June      | 07 July      | 07 May                 | 16 June      | 07 July      |
| 47                                               | 0,573                 | 0,569        | 0,570        | 0,085           | 0,090        | 0,089        | 0,104               | 0,100        | 0,102        | 0,070                  | 0,068        | 0,065        |
| 93                                               | 0,570                 | 0,560        | 0,556        | 0,085           | 0,087        | 0,085        | 0,101               | 0,096        | 0,098        | 0,073                  | 0,075        | 0,067        |
| 152                                              | 0,586                 | 0,537        | 0,570        | 0,081           | 0,086        | 0,087        | 0,101               | 0,096        | 0,098        | 0,075                  | 0,071        | 0,079        |
| <b>Mean</b>                                      | <b>0,576</b>          | <b>0,555</b> | <b>0,566</b> | <b>0,083</b>    | <b>0,088</b> | <b>0,087</b> | <b>0,102</b>        | <b>0,097</b> | <b>0,099</b> | <b>0,073</b>           | <b>0,071</b> | <b>0,070</b> |
| % Difference<br>(vs. 1 <sup>st</sup> . analysis) | —                     | -3,63 %      | -1,87 %      | —               | 4,91 %       | 4,19 %       | —                   | -4,80 %      | -2,96 %      | —                      | -2,17 %      | -3,10 %      |
| Diff (mean)                                      |                       | 0,021        | 0,011        |                 | 0,004        | 0,003        |                     | 0,005        | 0,003        |                        | 0,002        | 0,002        |
| 0,3* FFP-SD                                      |                       | 0,043        | 0,043        |                 | 0,006        | 0,006        |                     | 0,008        | 0,008        |                        | 0,005        | 0,005        |
| Judgement                                        |                       | passed       | passed       |                 | passed       | passed       |                     | passed       | passed       |                        | passed       | passed       |

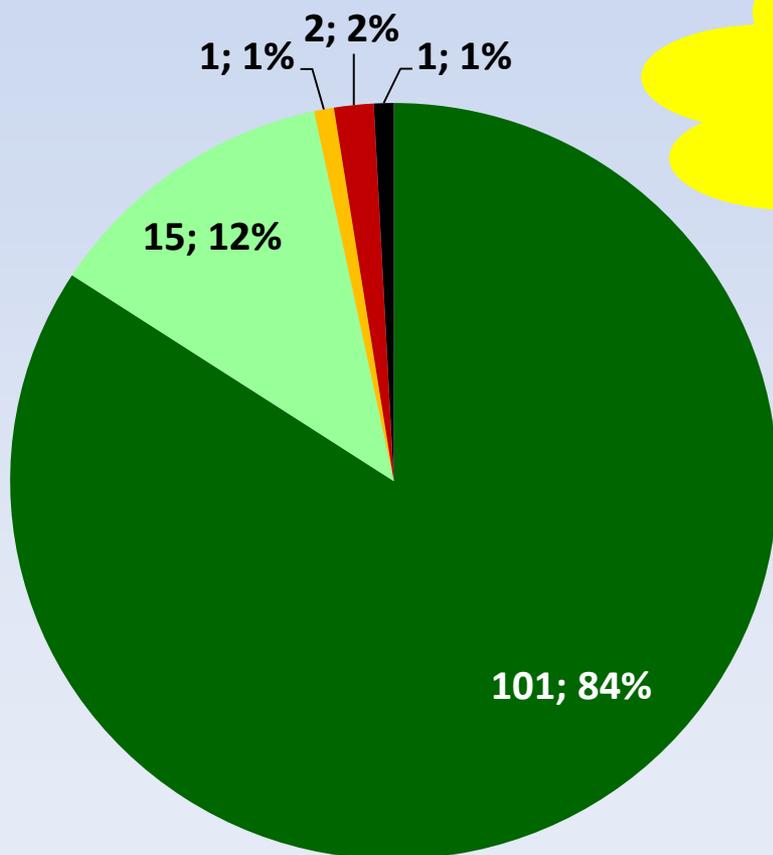
## OPTIONAL Compounds

| Sample                                        | Bentazone    |              |              | Bromoxynil   |              |              | N-Acetyl Glufosinate |              |              |
|-----------------------------------------------|--------------|--------------|--------------|--------------|--------------|--------------|----------------------|--------------|--------------|
|                                               | [mg/kg]      |              |              | [mg/kg]      |              |              | [mg/kg]              |              |              |
|                                               | 08 May       | 16 June      | 07 July      | 08 May       | 16 June      | 07 July      | 24 June              | 08 Aug       | 09 Sept      |
| 47                                            | 0,100        | 0,103        | 0,108        | 0,126        | 0,126        | 0,132        | 0,183                | 0,183        | 0,202        |
| 93                                            | 0,100        | 0,107        | 0,106        | 0,125        | 0,131        | 0,130        | 0,191                | 0,181        | 0,196        |
| 152                                           | 0,098        | 0,103        | 0,104        | 0,127        | 0,133        | 0,129        | 0,194                | 0,171        | 0,204        |
| <b>Mean</b>                                   | <b>0,099</b> | <b>0,105</b> | <b>0,106</b> | <b>0,126</b> | <b>0,130</b> | <b>0,130</b> | <b>0,189</b>         | <b>0,178</b> | <b>0,201</b> |
| % Difference (vs. 1 <sup>st</sup> . analysis) | —            | 5,36 %       | 6,84 %       | —            | 3,20 %       | 3,53 %       | —                    | -5,82 %      | 6,09 %       |
| Diff (mean)                                   |              | 0,005        | 0,007        |              | 0,004        | 0,004        |                      | 0,011        | 0,012        |
| 0,3* FFP-SD                                   |              | 0,007        | 0,007        |              | 0,009        | 0,009        |                      | 0,014        | 0,014        |
| Judgement                                     |              | passed       | passed       |              | passed       | passed       |                      | passed       | passed       |

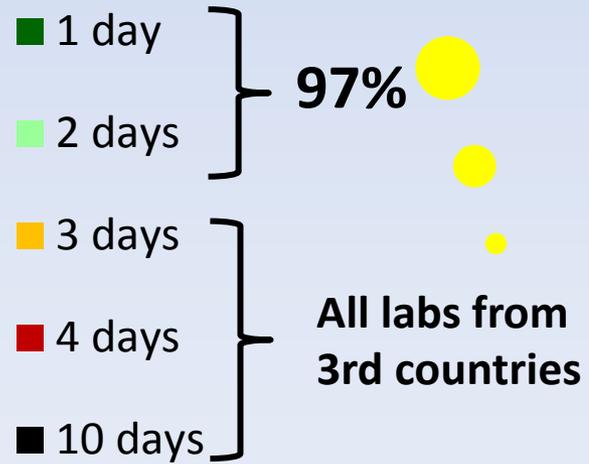
| Sample                                        | Phosphonic acid |              |              | TFNG         |              |              |  |  |  |
|-----------------------------------------------|-----------------|--------------|--------------|--------------|--------------|--------------|--|--|--|
|                                               | [mg/kg]         |              |              | [mg/kg]      |              |              |  |  |  |
|                                               | 07 May          | 16 June      | 07 July      | 08 May       | 16 June      | 07 July      |  |  |  |
| 47                                            | 0,721           | 0,719        | 0,722        | 0,167        | 0,164        | 0,157        |  |  |  |
| 93                                            | 0,693           | 0,727        | 0,736        | 0,167        | 0,165        | 0,162        |  |  |  |
| 152                                           | 0,731           | 0,730        | 0,736        | 0,166        | 0,162        | 0,149        |  |  |  |
| <b>Mean</b>                                   | <b>0,715</b>    | <b>0,725</b> | <b>0,731</b> | <b>0,167</b> | <b>0,164</b> | <b>0,156</b> |  |  |  |
| % Difference (vs. 1 <sup>st</sup> . analysis) | —               | 1,44 %       | 2,25 %       | —            | -1,80 %      | -6,34 %      |  |  |  |
| Diff (mean)                                   |                 | 0,010        | 0,016        |              | 0,003        | 0,011        |  |  |  |
| 0,3* FFP-SD                                   |                 | 0,054        | 0,054        |              | 0,012        | 0,012        |  |  |  |
| Judgement                                     |                 | passed       | passed       |              | passed       | passed       |  |  |  |

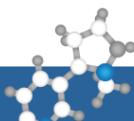


# Shipping Duration



**Q: Is there any significant degradation taking place during shipment?**

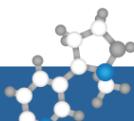




## COMPULSORY Compounds

|                  | Temp. of Test Item | 2,4-D                            | Chlor-mequat | Dithios | Ethephon | Glypho-sate | MCPA  | Mepiquat | Propamo-carb |
|------------------|--------------------|----------------------------------|--------------|---------|----------|-------------|-------|----------|--------------|
|                  |                    | Mean Concentration @ n=3 [mg/kg] |              |         |          |             |       |          |              |
| Day 0            | ~ - 5°C            | 0,103                            | 0,153        | 0,706   | 0,164    | 0,581       | 0,089 | 0,103    | 0,079        |
| Day 2            | ~ 16°C             | 0,098                            | 0,146        | 0,771   | 0,154    | 0,584       | 0,088 | 0,100    | 0,073        |
| Day 4            | RT                 | 0,095                            | 0,143        | 0,715   | 0,151    | 0,562       | 0,081 | 0,102    | 0,070        |
| Day 10           | RT                 | 0,095                            | 0,145        | 0,581   | 0,148    | 0,594       | 0,085 | 0,099    | 0,067        |
| Deviation [%]    |                    |                                  |              |         |          |             |       |          |              |
| Day 2 vs. Day 0  |                    | -5,2%                            | -4,3%        | 9,2%    | -6,2%    | 0,6%        | -1,5% | -2,7%    | -7,5%        |
| Day 4 vs. Day 0  |                    | -7,5%                            | -6,4%        | 1,2%    | -7,9%    | -3,2%       | -9,0% | -0,8%    | -11,5%       |
| Day 10 vs. Day 0 |                    | -7,4%                            | -5,2%        | -17,8%  | -9,8%    | 2,2%        | -4,3% | -4,1%    | -14,7%       |

**Packed exactly the same way as the Test Items  
(deep frozen in insulated styrofoam box, left at ambient temperature).**



## OPTIONAL Compounds

|                  | Temp. of Test Item | Bentazone                        | Bromoxynil | N-acetyl-Glufosinate | Phosphonic acid | TFNG   |
|------------------|--------------------|----------------------------------|------------|----------------------|-----------------|--------|
|                  |                    | Mean Concentration @ n=3 [mg/kg] |            |                      |                 |        |
| Day 0            | ~ - 5°C            | 0,110                            | 0,134      | 0,193                | 0,718           | 0,169  |
| Day 2            | ~ 16°C             | 0,102                            | 0,130      | 0,184                | 0,752           | 0,165  |
| Day 4            | RT                 | 0,100                            | 0,129      | 0,183                | 0,725           | 0,160  |
| Day 10           | RT                 | 0,095                            | 0,122      | 0,192                | 0,725           | 0,144  |
| Deviation [%]    |                    |                                  |            |                      |                 |        |
| Day 2 vs. Day 0  |                    | -6,9%                            | -2,7%      | -5,0%                | 4,7%            | -2,4%  |
| Day 4 vs. Day 0  |                    | -8,9%                            | -3,3%      | -5,1%                | 1,1%            | -5,5%  |
| Day 10 vs. Day 0 |                    | -13,4%                           | -8,7%      | -0,5%                | 1,0%            | -14,7% |

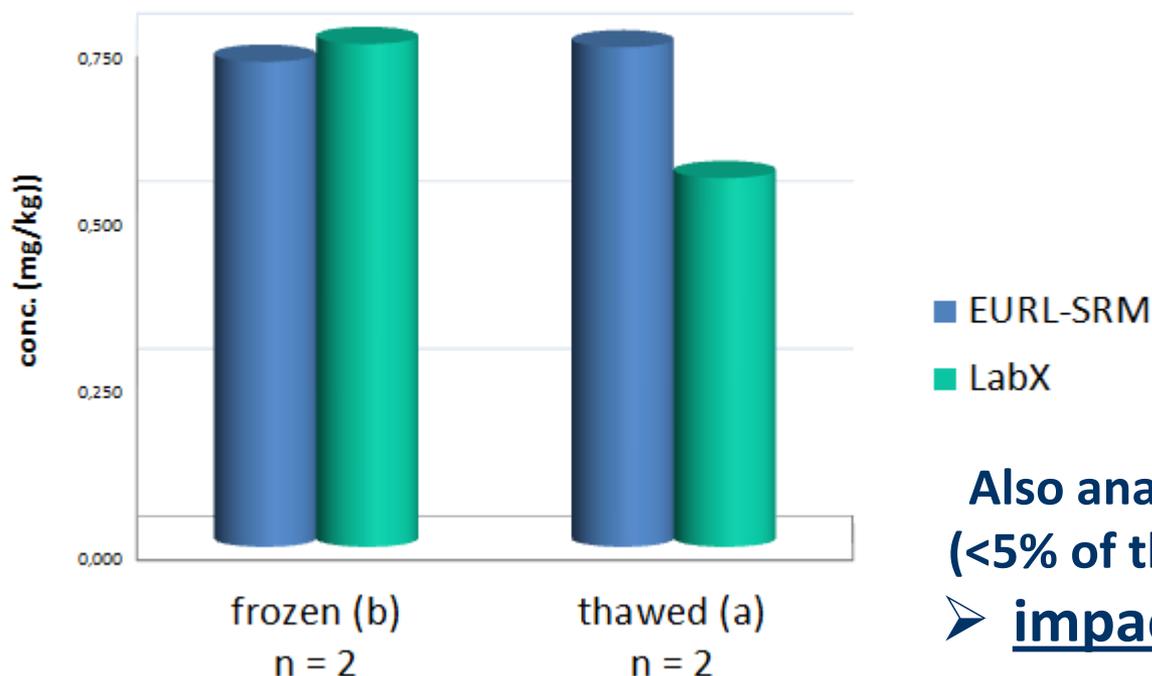
**Packed exactly the same way as the Test Items  
(deep frozen in insulated styrofoam box, left at ambient temperature).**

1 Lab reported :

> 50 % DTC-losses when sample was left for 19h in fridge

EURL-SRM investigated:

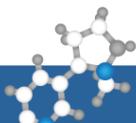
### Dithiocarbamates in EUPT-SRM10 Corn

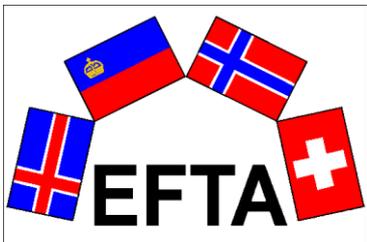


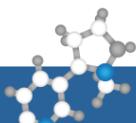
### Treatment of samples:

|     |                         |
|-----|-------------------------|
| (a) | samples at 4 °C for 19h |
| (b) | samples at -20 °C       |

Also analyzed free CS<sub>2</sub> -> Low levels (<5% of the total CS<sub>2</sub>, after hydrolysis)  
 ➤ impact of volatilization is low



|                                           |                                                                                    | Labs submitting results | Registered WITHOUT submitting results |
|-------------------------------------------|------------------------------------------------------------------------------------|-------------------------|---------------------------------------|
| EU                                        |   | 102                     | 8                                     |
| EFTA                                      |   | 2                       | -                                     |
| 3 <sup>rd</sup> Countries + EU Candidates |  | 6                       | -                                     |
| <b>SUM</b>                                |                                                                                    | <b>110</b>              | <b>8</b>                              |



| EU Country<br>(Contracting) | Registered for PT |           | Submitted results |           |
|-----------------------------|-------------------|-----------|-------------------|-----------|
|                             | Total             | NRL-SRM   | Total             | NRL       |
| AT                          | 2                 | 1         | 2                 | 1         |
| BE                          | 5                 | 1         | 3                 | 1         |
| BE / DE                     | 1                 |           | 1                 |           |
| BE/ FR / LU                 | 1                 |           | 1                 |           |
| BG                          | 3                 | 1         | 2                 | 1         |
| HR                          | 2                 |           | 2                 |           |
| CY                          | 1                 | 1         | 1                 | 1         |
| CZ                          | 3                 | 1         | 3                 | 1         |
| FR                          | 8                 | 1         | 8                 | 1         |
| DE                          | 22                | 1         | 22                | 1         |
| DK                          | 2                 | 1         | 2                 | 1         |
| EE                          | 2                 | 1         | 2                 | 1         |
| FI                          | 1                 | 1         | 1                 | 1         |
| GR                          | 2                 | 2         | 2                 | 2         |
| HU                          | 4                 | 1         | 4                 | 1         |
| IE                          | 1                 | 1         | 1                 | 1         |
| IT                          | 11                | 1         | 8                 | 1         |
| LT                          | 2                 | 1         | 2                 | 1         |
| LU                          | 1                 | 1         | 1                 | 1         |
| LV                          | 1                 | 1         | 1                 | 1         |
| MT*                         | 1                 | *         | 1                 |           |
| NL                          | 2                 | 1         | 2                 | 1         |
| PL                          | 7                 | 1         | 7                 | 1         |
| PT                          | 2                 | 1         | 2                 | 1         |
| RO                          | 1                 |           | 1                 |           |
| ES                          | 13                | 2         | 11                | 2         |
| ES / MT                     | 1                 |           | 1                 |           |
| SE                          | 2                 | 1         | 2                 | 1         |
| SI                          | 3                 | 1         | 3                 | 1         |
| SK                          | 1                 | 1         | 1                 | 1         |
| UK / MT                     | 2                 | 1*        | 2                 | 1         |
| <b>EU-Total</b>             | <b>110</b>        | <b>27</b> | <b>102</b>        | <b>27</b> |

| Countries                                | Registered for PT | Submitted results |
|------------------------------------------|-------------------|-------------------|
| Norway                                   | 1                 | 1                 |
| Switzerland                              | 1                 | 1                 |
| <b>EFTA-Total</b>                        | <b>2</b>          | <b>2</b>          |
| Australia                                | 2                 | 2                 |
| Egypt                                    | 1                 | 1                 |
| Serbia                                   | 1                 | 1                 |
| Singapore                                | 1                 | 1                 |
| Canada                                   | 1                 | 1                 |
| <b>3rd Countries<br/>+ EU-Candidates</b> | <b>6</b>          | <b>6</b>          |

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

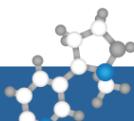
FytoLab (BE): Subcontracted by BE, FR, LU

LUFA (DE): Subcontracted by BE, DE

Countries with no NRL-SRMs participating:

HR "NRL-SRM not yet appointed"

RO "not single methods in the routine controls"



## Compulsory compounds

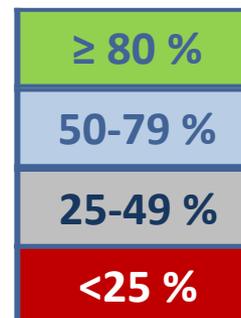
### Compounds Present in Test Item

| Compound         | No. of Labs targeting | % (out of 104* labs) |
|------------------|-----------------------|----------------------|
| Propamocarb      | 87                    | 84%                  |
| Dithiocarbamates | 86                    | 83%                  |
| 2,4-D            | 82                    | 79%                  |
| MCPA             | 80                    | 77%                  |
| Mepiquat         | 76                    | 73%                  |
| Chlormequat      | 75                    | 72%                  |
| Glyphosate       | 64                    | 62%                  |
| Ethephon         | 61                    | 59%                  |

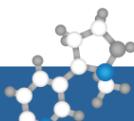
### NOT present

| Compound         | No. of Labs targeting | % (out of 104* labs) |
|------------------|-----------------------|----------------------|
| Fenbutatin Oxide | 56                    | 54%                  |

### Coverage



\*: 102 EU + 2 EFTA labs submitting results



## Optional Compounds

### Present in Test Item

| Compounds              | No. of Labs targeting | % (out of 104* labs) |
|------------------------|-----------------------|----------------------|
| Bentazone**            | 69                    | 66%                  |
| Bromoxynil**           | 65                    | 63%                  |
| TFNG**                 | 30                    | 29%                  |
| Phosphonic acid**      | 25                    | 24%                  |
| N-Acetyl Glufosinate** | 16                    | 15%                  |

### NOT present in Test Item

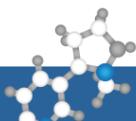
| Compounds    | No. of Labs targeting | % (out 104* labs) |
|--------------|-----------------------|-------------------|
| 2,4-DP       | 71                    | 68%               |
| MCPP         | 69                    | 66%               |
| Ioxynil**    | 66                    | 63%               |
| Fluroxypyr** | 62                    | 60%               |
| Dicamba      | 41                    | 39%               |
| Glufosinate  | 33                    | 32%               |
| TFNA**       | 30                    | 29%               |
| Paraquat     | 16                    | 15%               |
| MPP**        | 14                    | 13%               |

### Coverage

|         |
|---------|
| ≥ 80 %  |
| 50-79 % |
| 25-49 % |
| <25 %   |

\*: 102 EU + 2 EFTA labs submitting results

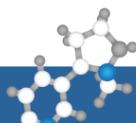
\*\* : Analytes first time in the EUPT-SRM



False Negatives (FNs) = 6

EU+EFTA

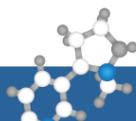
| Compound   |                         | MRRL<br>[mg/kg] | Assigned<br>Value<br>[mg/kg] | No.<br>FNs | Method                          | Lab<br>Code | RL<br>[mg/kg] |
|------------|-------------------------|-----------------|------------------------------|------------|---------------------------------|-------------|---------------|
| COMPULSORY | Dithios                 | 0.05            | 0.559                        | 1          | SnCl <sub>2</sub> /HCL-cleavage | 95          | 0.05          |
|            | Glyphosate              | 0.05            | 0.568                        | 2          | deriv. w. FMOC                  | 13          | 0.01          |
|            |                         |                 |                              |            | QuPpe                           | 26          | 0.5           |
|            | MCPA                    | 0.01            | 0.081                        | 1          | QuEChERS                        | 1           | 0.01          |
| OPTIONAL   | N-Acetyl<br>Glufosinate | 0.02            | 0.319                        | 1          | QuPpe                           | 60<br>(NRL) | 0.04          |
|            | Phosphonic<br>acid      | 0.05            | 0.584                        | 1          | QuPpe                           | 27<br>(NRL) | 0.05          |



**False Positives (FP) = 4**

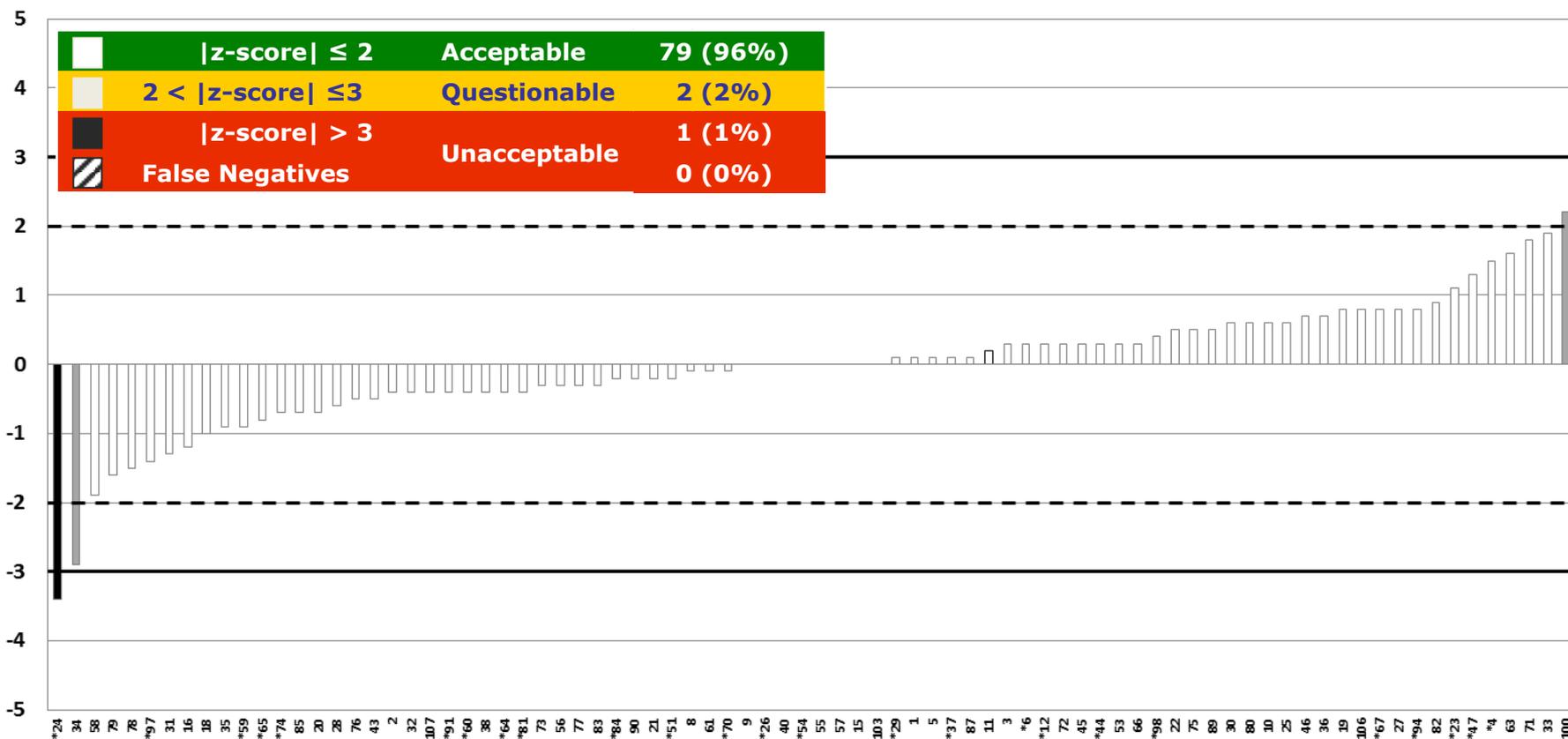
**EU+EFTA**

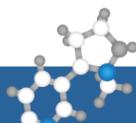
| Compound |             | No. of FP | Lab Code | RL [mg/kg] | Results [mg/kg] |
|----------|-------------|-----------|----------|------------|-----------------|
| OPTIONAL | Glufosinate | 3         | 8        | 0.05       | 0.105           |
|          |             |           | 72       | 0.02       | 0.209           |
|          |             |           | 91 (NRL) | 0.02       | 0.167           |
|          | MPP         | 1         | 8        | 0.01       | 0.058           |



# 2,4-D (free acid)

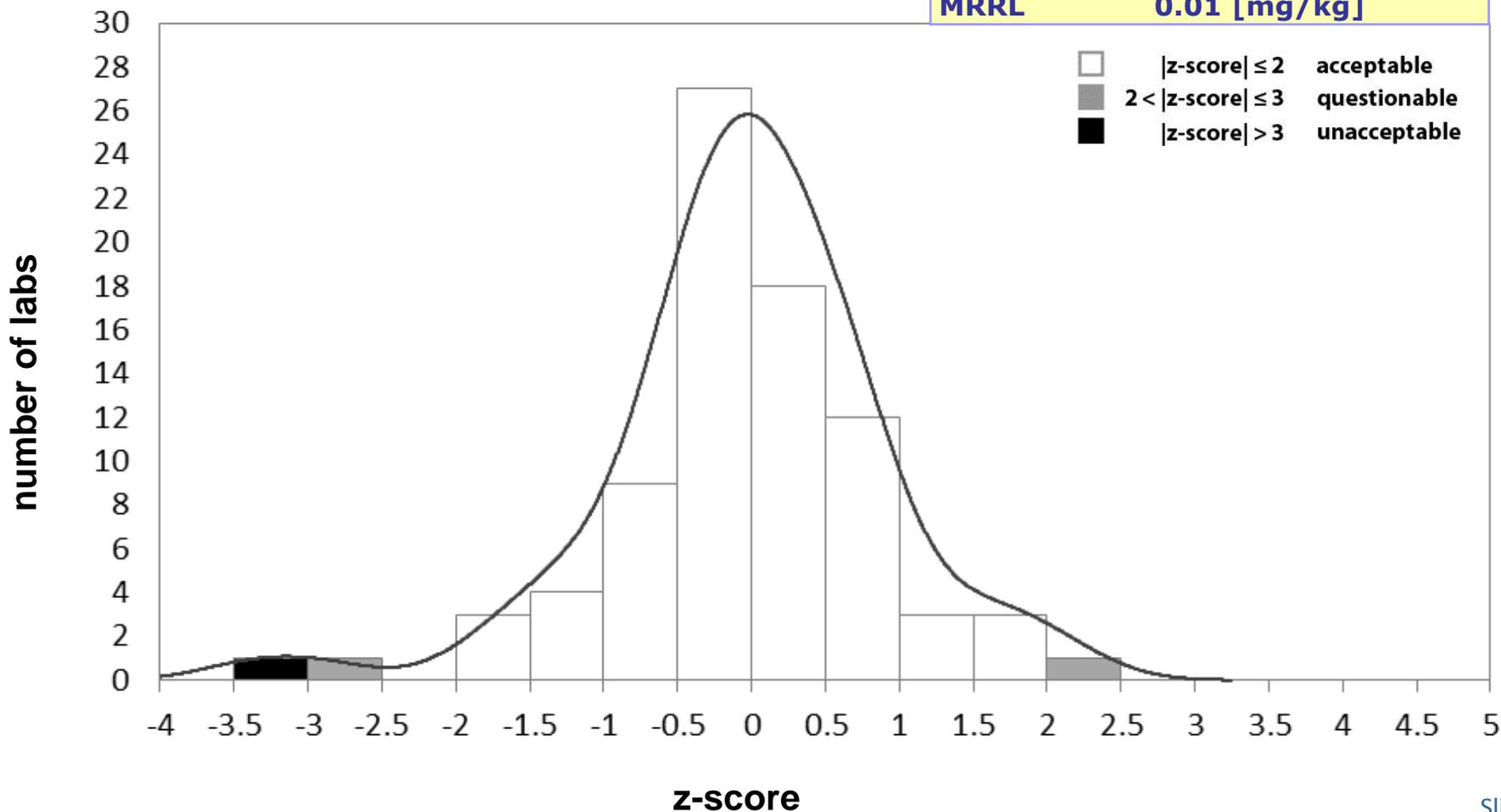
|                    |                      |
|--------------------|----------------------|
| <b>Results</b>     | <b>82</b>            |
| <b>False Neg.</b>  | <b>0</b>             |
| <b>Robust Mean</b> | <b>0.092 [mg/kg]</b> |
| <b>Robust RSD</b>  | <b>18.2 %</b>        |
| <b>MRRL</b>        | <b>0.01 [mg/kg]</b>  |

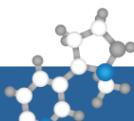




# 2,4-D (free acid)

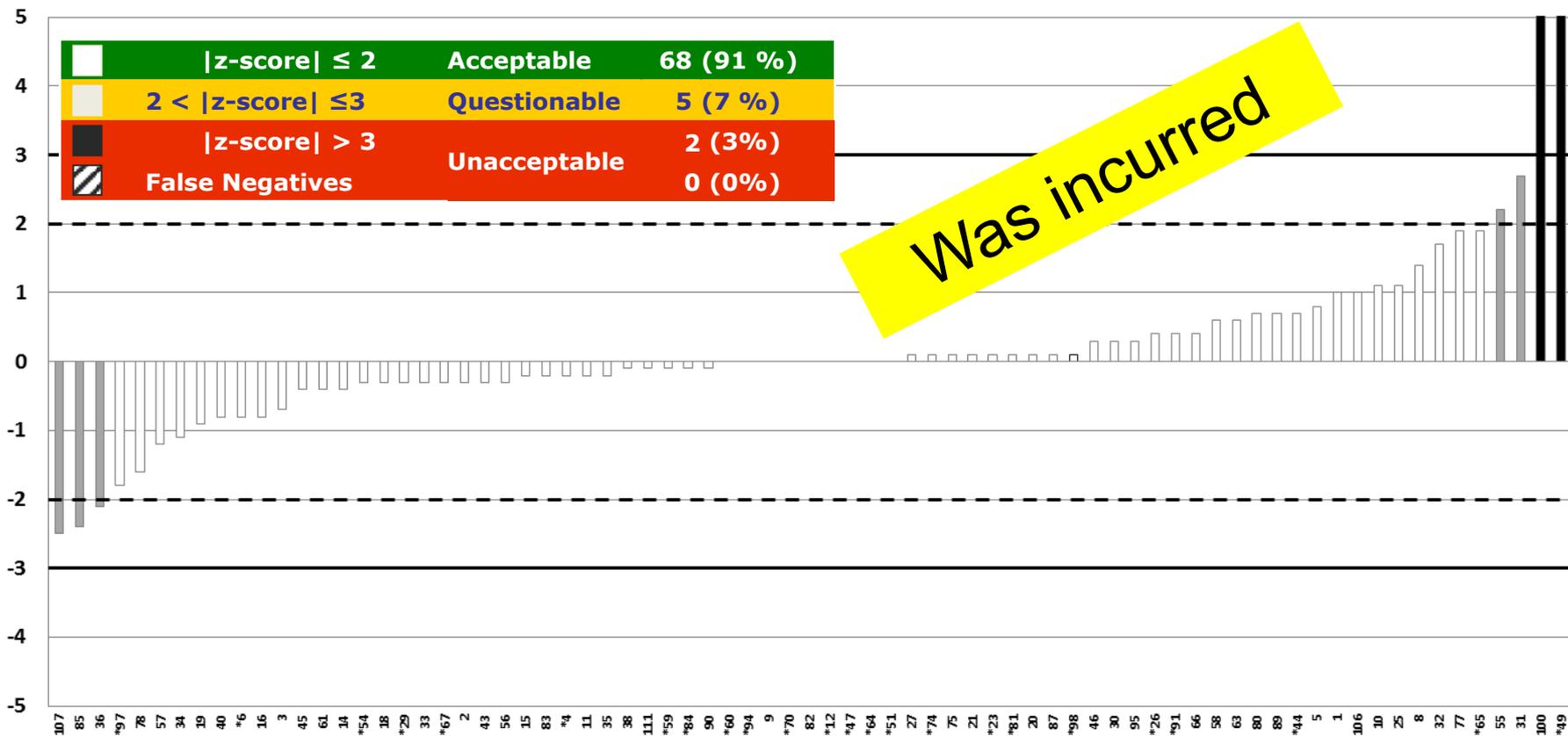
|                    |                      |
|--------------------|----------------------|
| <b>Results</b>     | <b>82</b>            |
| <b>False Neg.</b>  | <b>0</b>             |
| <b>Robust Mean</b> | <b>0.092 [mg/kg]</b> |
| <b>Robust RSD</b>  | <b>18.2 %</b>        |
| <b>MRRL</b>        | <b>0.01 [mg/kg]</b>  |

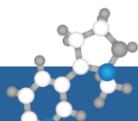




# CHLORMEQUAT

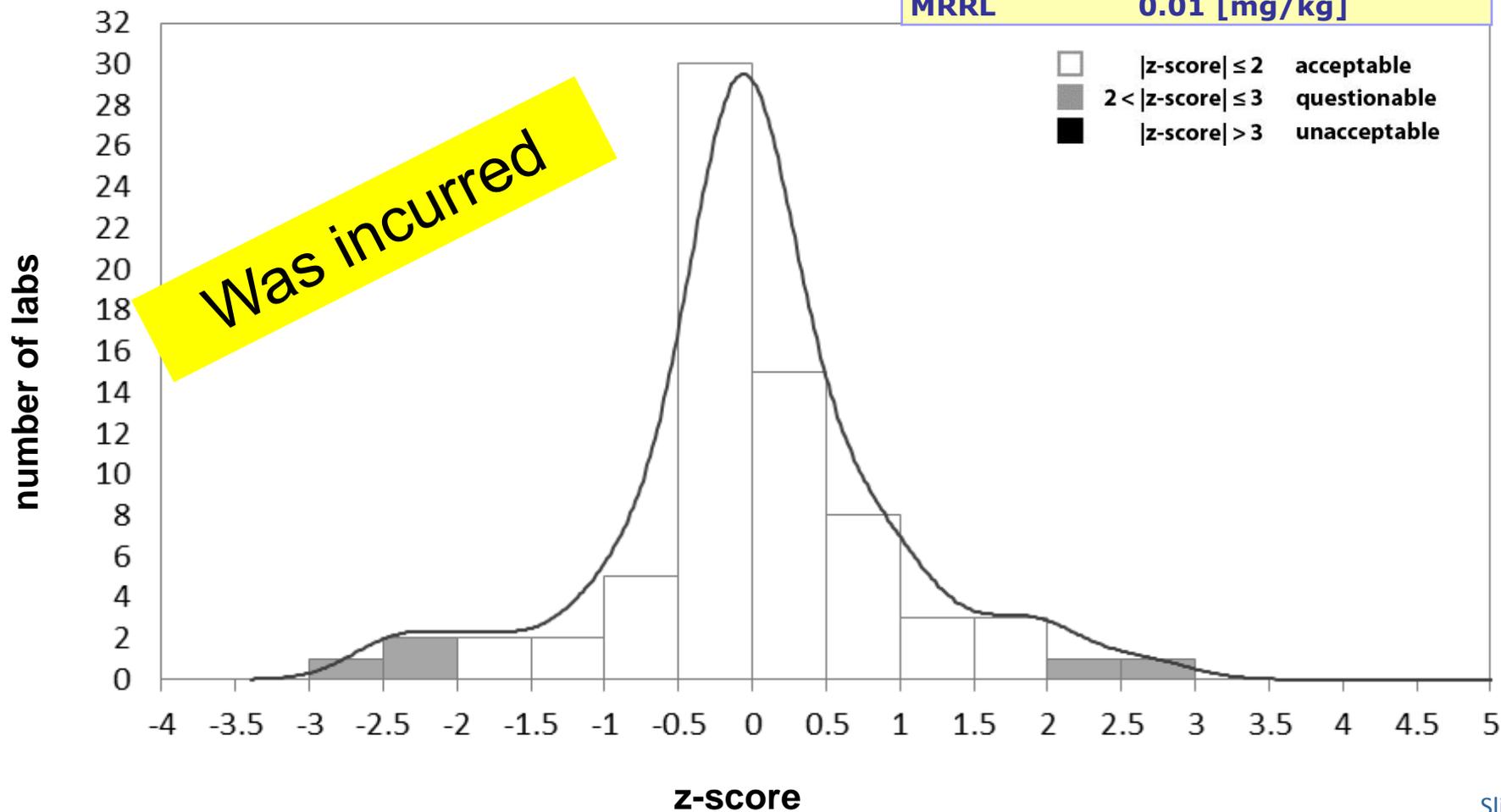
|                    |                      |
|--------------------|----------------------|
| <b>Results</b>     | <b>75</b>            |
| <b>False Neg.</b>  | <b>0</b>             |
| <b>Robust Mean</b> | <b>0.167 [mg/kg]</b> |
| <b>Robust RSD</b>  | <b>18.2 %</b>        |
| <b>MRRL</b>        | <b>0.01 [mg/kg]</b>  |





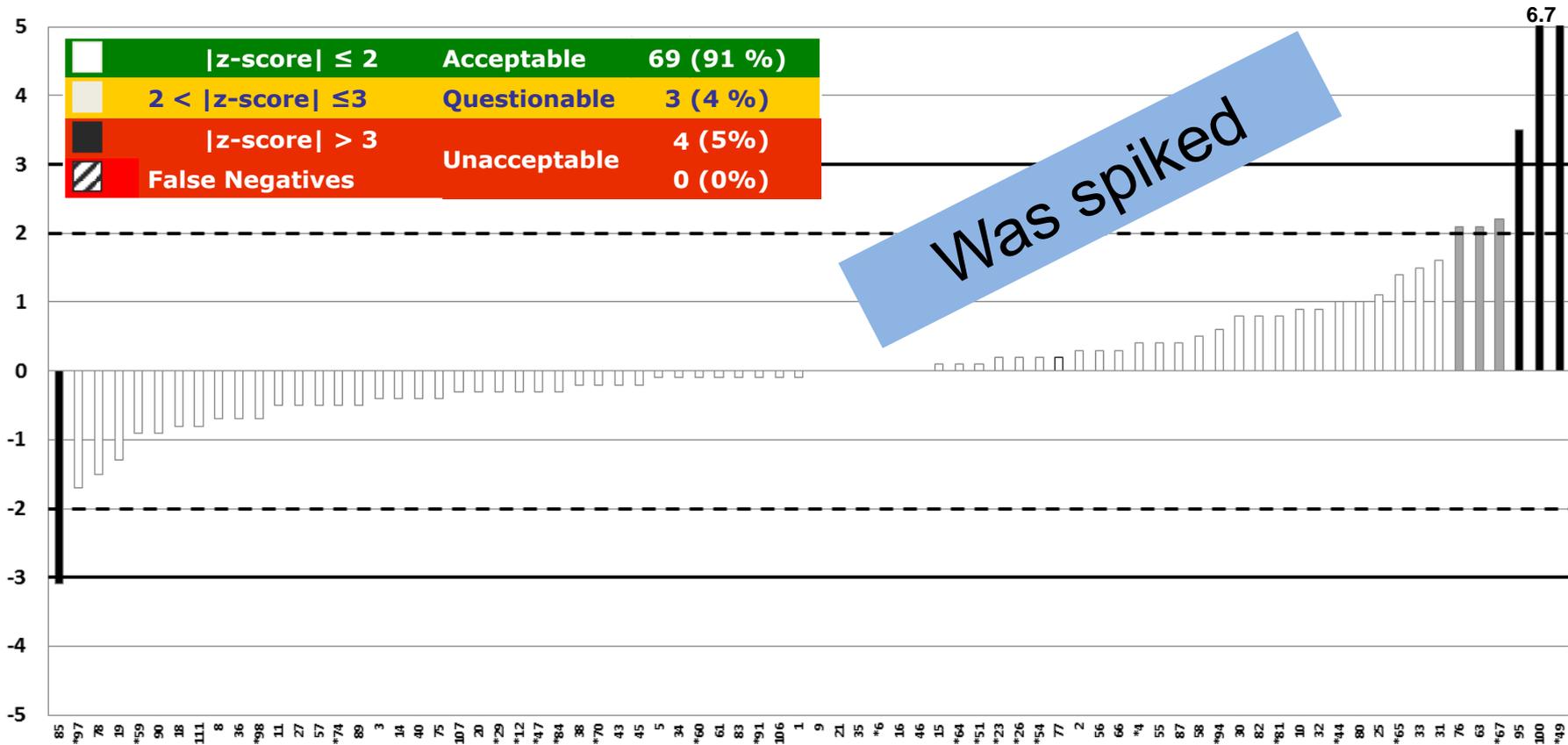
# CHLORMEQUAT

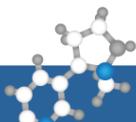
|                    |                      |
|--------------------|----------------------|
| <b>Results</b>     | <b>75</b>            |
| <b>False Neg.</b>  | <b>0</b>             |
| <b>Robust Mean</b> | <b>0.167 [mg/kg]</b> |
| <b>Robust RSD</b>  | <b>18.2 %</b>        |
| <b>MRRL</b>        | <b>0.01 [mg/kg]</b>  |



# MEPIQUAT

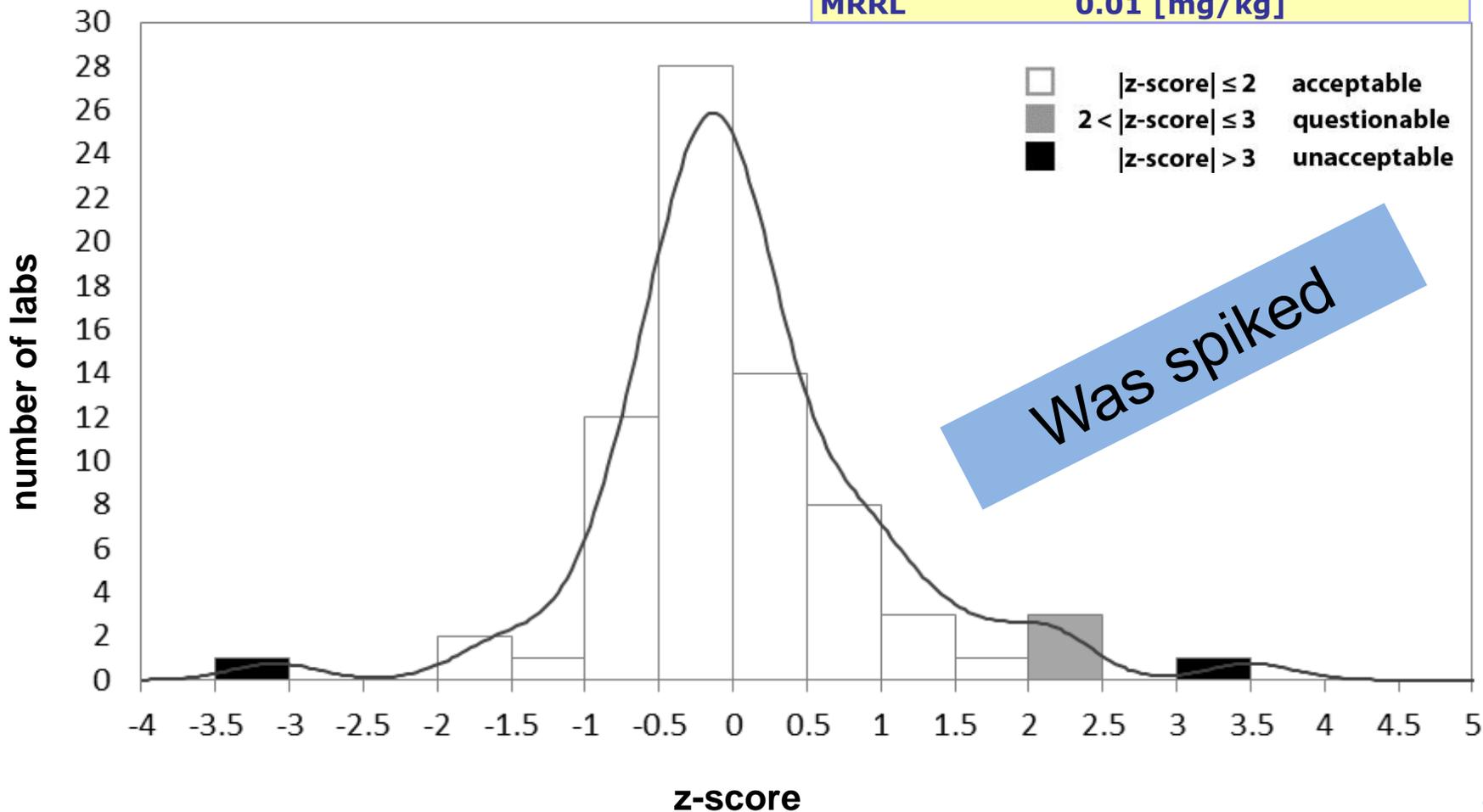
|             |               |
|-------------|---------------|
| Results     | 76            |
| False Neg.  | 0             |
| Robust Mean | 0.114 [mg/kg] |
| Robust RSD  | 18.5 %        |
| MRRL        | 0.01 [mg/kg]  |

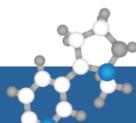




# MEPIQUAT

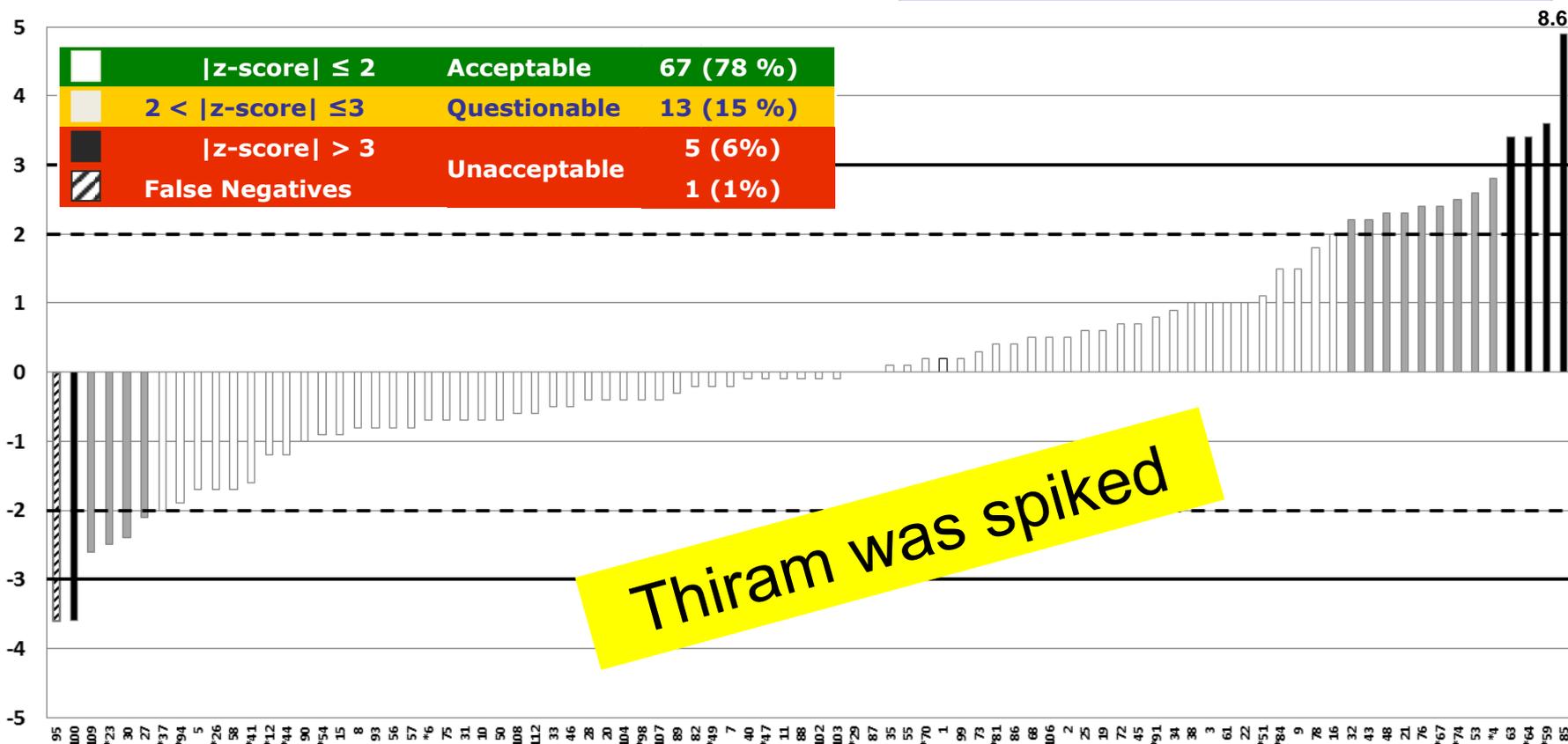
|                    |                      |
|--------------------|----------------------|
| <b>Results</b>     | <b>76</b>            |
| <b>False Neg.</b>  | <b>0</b>             |
| <b>Robust Mean</b> | <b>0.114 [mg/kg]</b> |
| <b>Robust RSD</b>  | <b>18.5 %</b>        |
| <b>MRRL</b>        | <b>0.01 [mg/kg]</b>  |

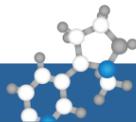




# Dithiocarbamates

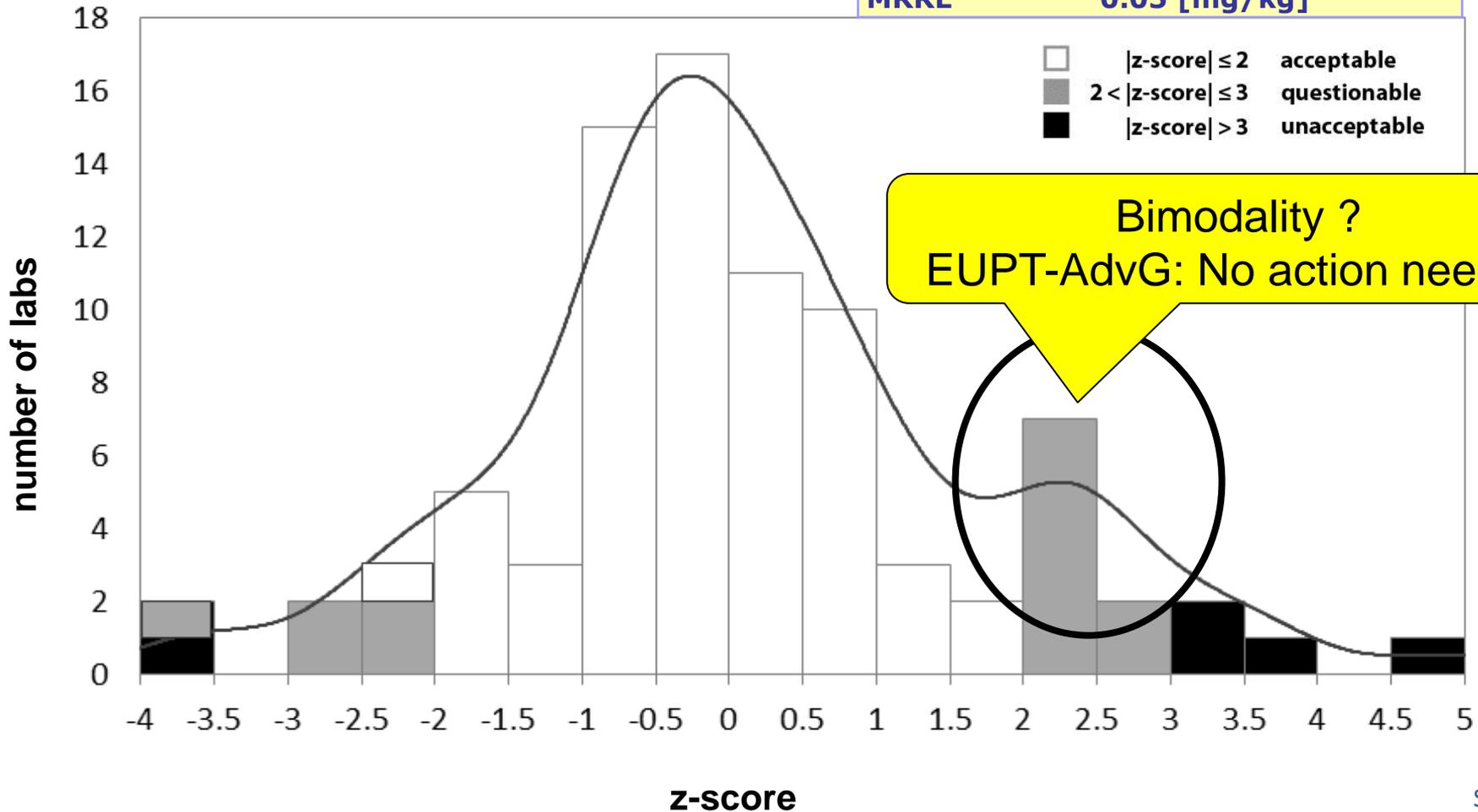
|             |               |
|-------------|---------------|
| Results     | 85            |
| False Neg.  | 1             |
| Robust Mean | 0.559 [mg/kg] |
| Robust RSD  | 36.9 %        |
| MRRL        | 0.05 [mg/kg]  |

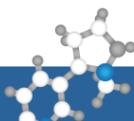




# Dithiocarbamates

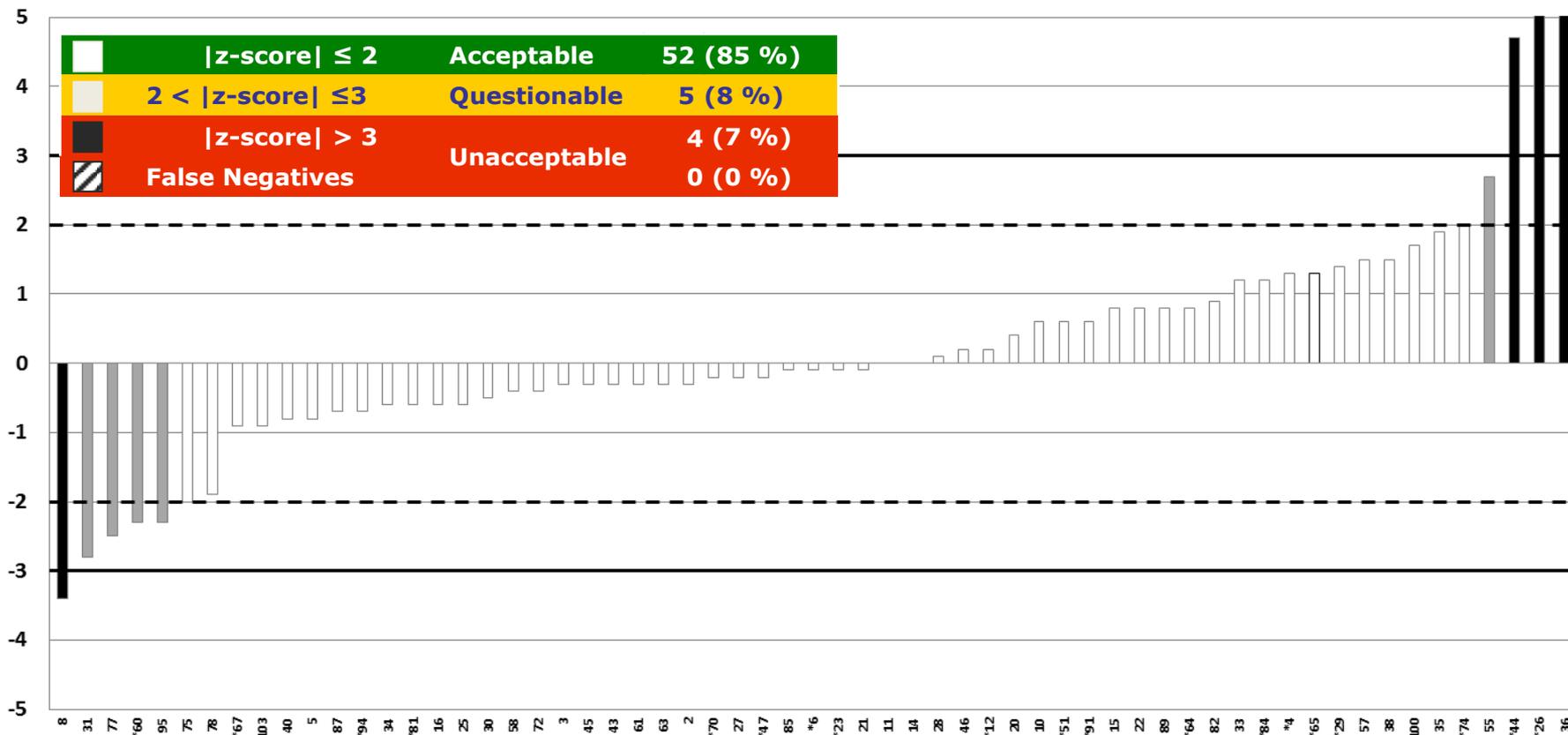
|                    |                      |
|--------------------|----------------------|
| <b>Results</b>     | <b>85</b>            |
| <b>False Neg.</b>  | <b>1</b>             |
| <b>Robust Mean</b> | <b>0.559 [mg/kg]</b> |
| <b>Robust RSD</b>  | <b>36.9 %</b>        |
| <b>MRRL</b>        | <b>0.05 [mg/kg]</b>  |

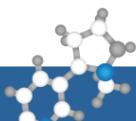




|                    |                      |
|--------------------|----------------------|
| <b>Results</b>     | <b>61</b>            |
| <b>False Neg.</b>  | <b>0</b>             |
| <b>Robust Mean</b> | <b>0.162 [mg/kg]</b> |
| <b>Robust RSD</b>  | <b>30.8 %</b>        |
| <b>MRRL</b>        | <b>0.02 [mg/kg]</b>  |

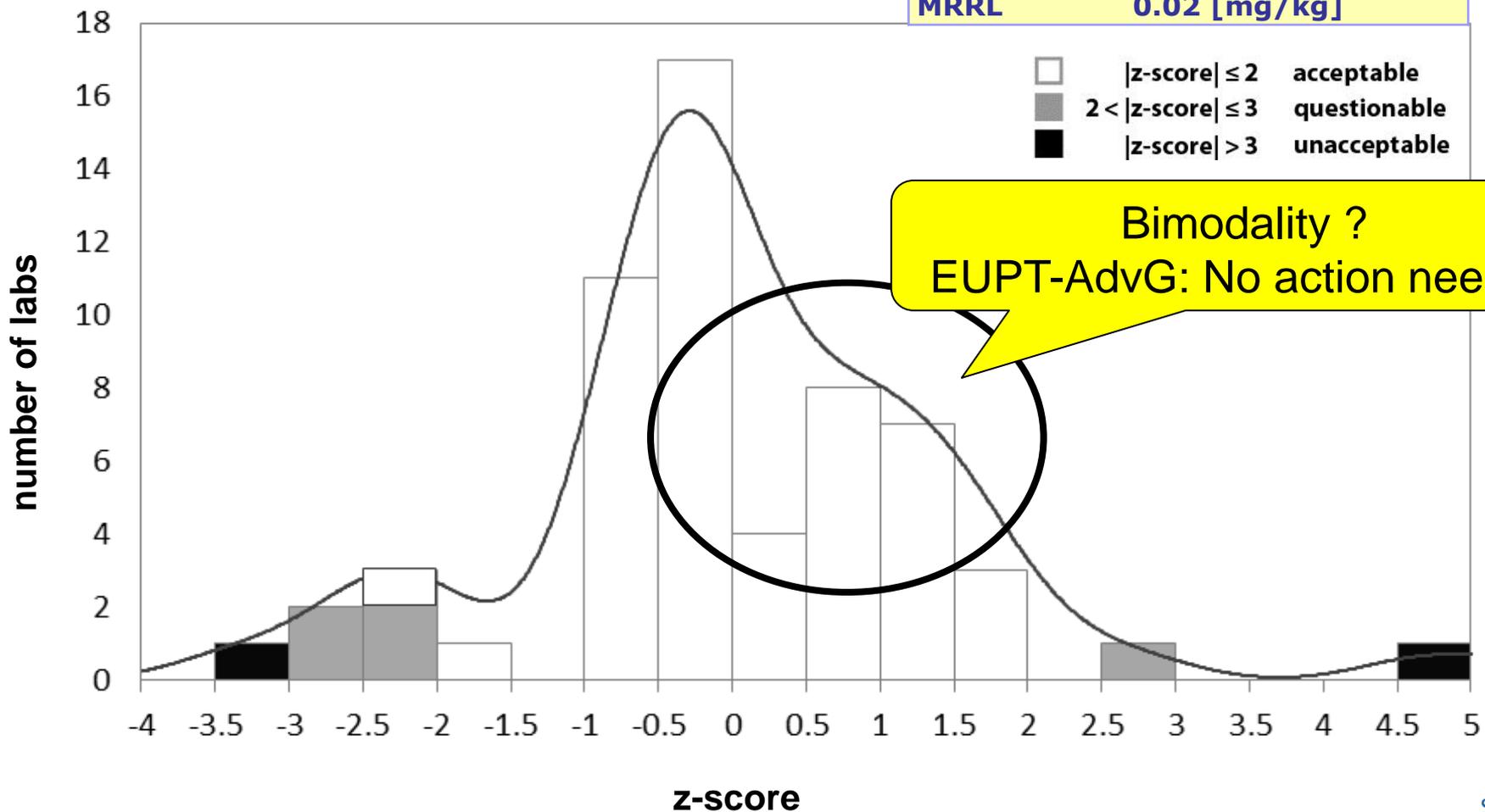
# ETHEPHON

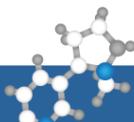




|                    |                      |
|--------------------|----------------------|
| <b>Results</b>     | <b>61</b>            |
| <b>False Neg.</b>  | <b>0</b>             |
| <b>Robust Mean</b> | <b>0.162 [mg/kg]</b> |
| <b>Robust RSD</b>  | <b>30.8 %</b>        |
| <b>MRRL</b>        | <b>0.02 [mg/kg]</b>  |

# ETHEPHON

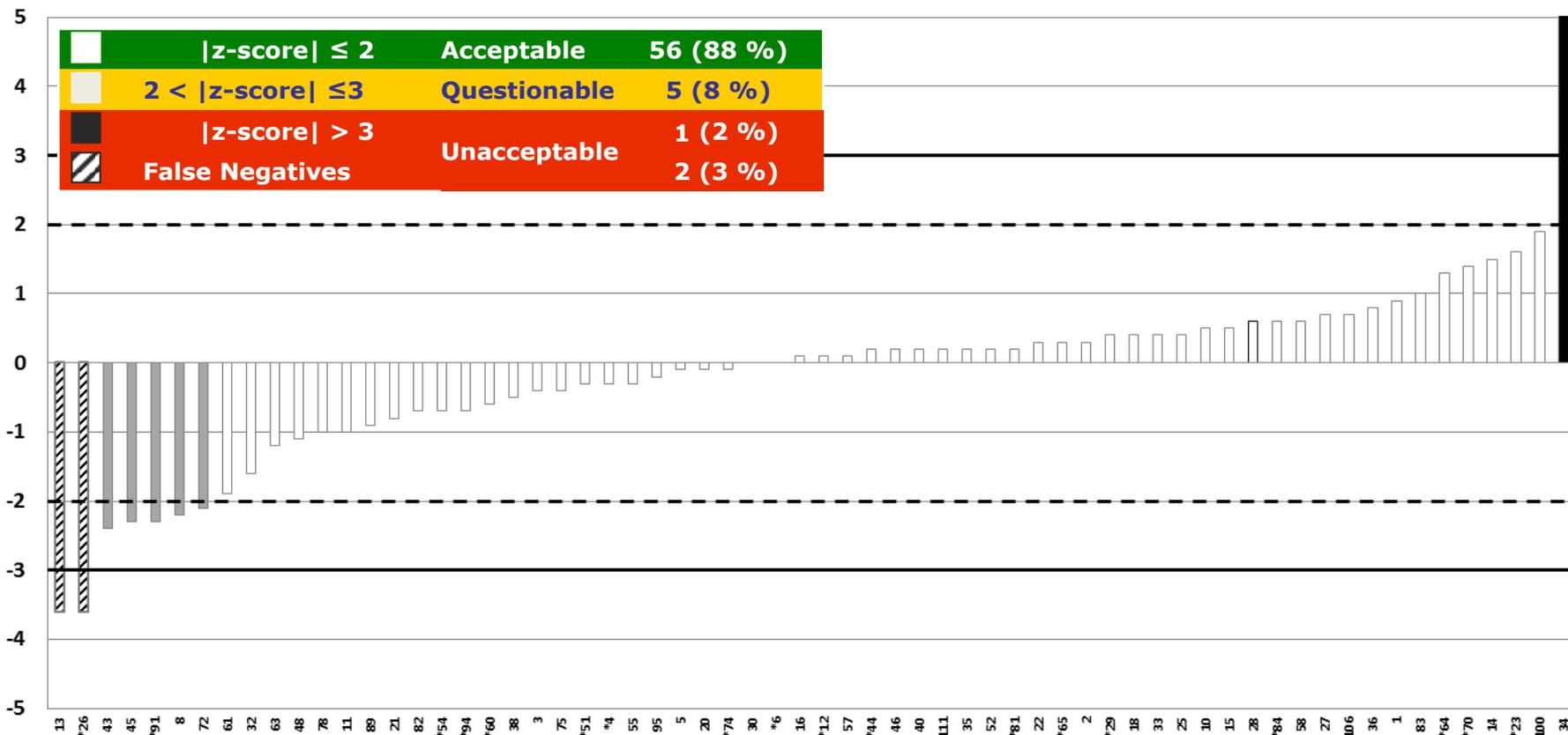


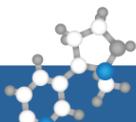


# GLYPHOSATE

**Was incurred**

|                    |                      |
|--------------------|----------------------|
| <b>Results</b>     | <b>62</b>            |
| <b>False Neg.</b>  | <b>2</b>             |
| <b>Robust Mean</b> | <b>0.568 [mg/kg]</b> |
| <b>Robust RSD</b>  | <b>22.8 %</b>        |
| <b>MRRL</b>        | <b>0.05 [mg/kg]</b>  |

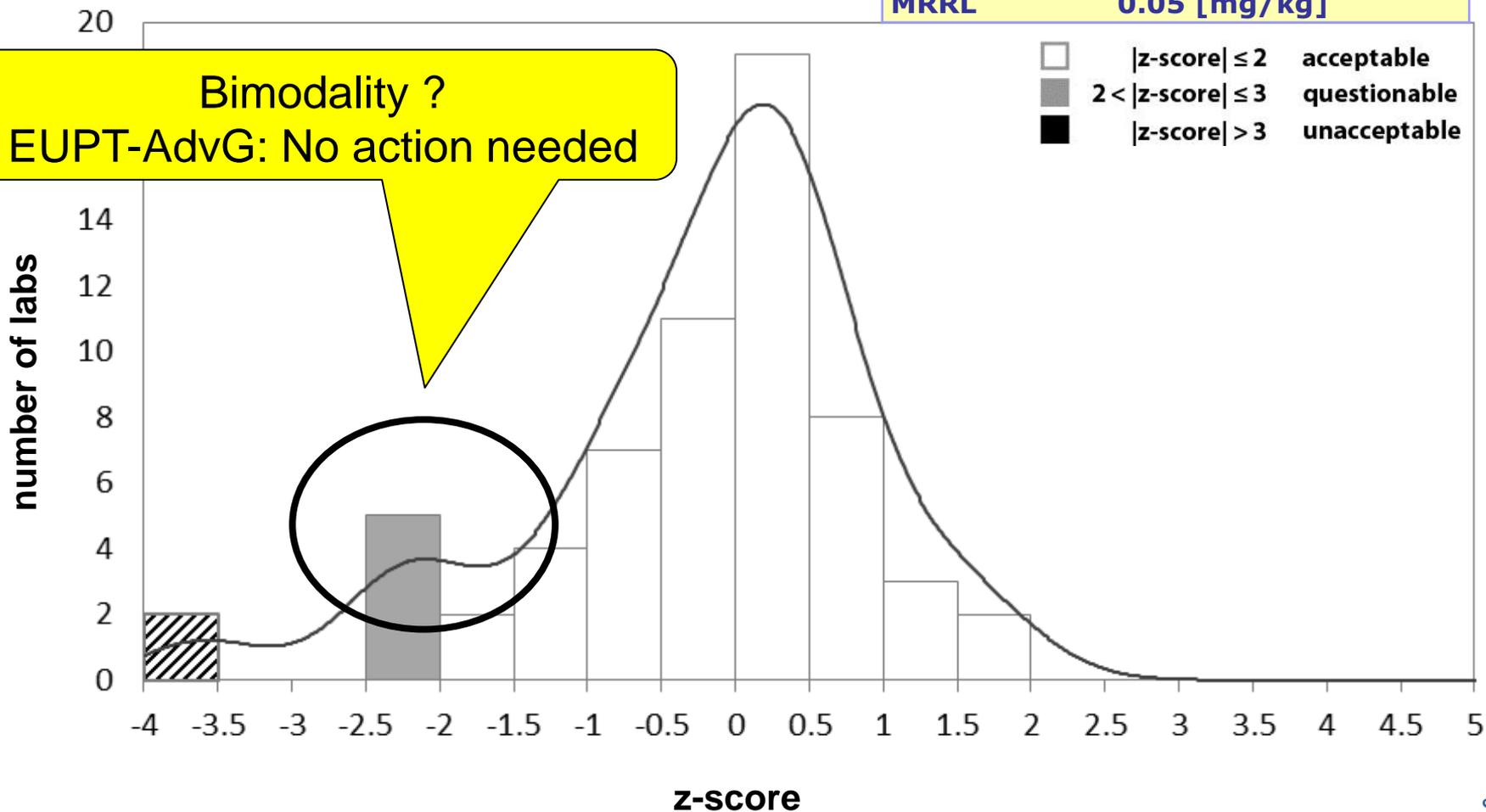


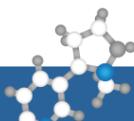


|                    |                      |
|--------------------|----------------------|
| <b>Results</b>     | <b>62</b>            |
| <b>False Neg.</b>  | <b>2</b>             |
| <b>Robust Mean</b> | <b>0.568 [mg/kg]</b> |
| <b>Robust RSD</b>  | <b>22.8 %</b>        |
| <b>MRRL</b>        | <b>0.05 [mg/kg]</b>  |

# GLYPHOSATE

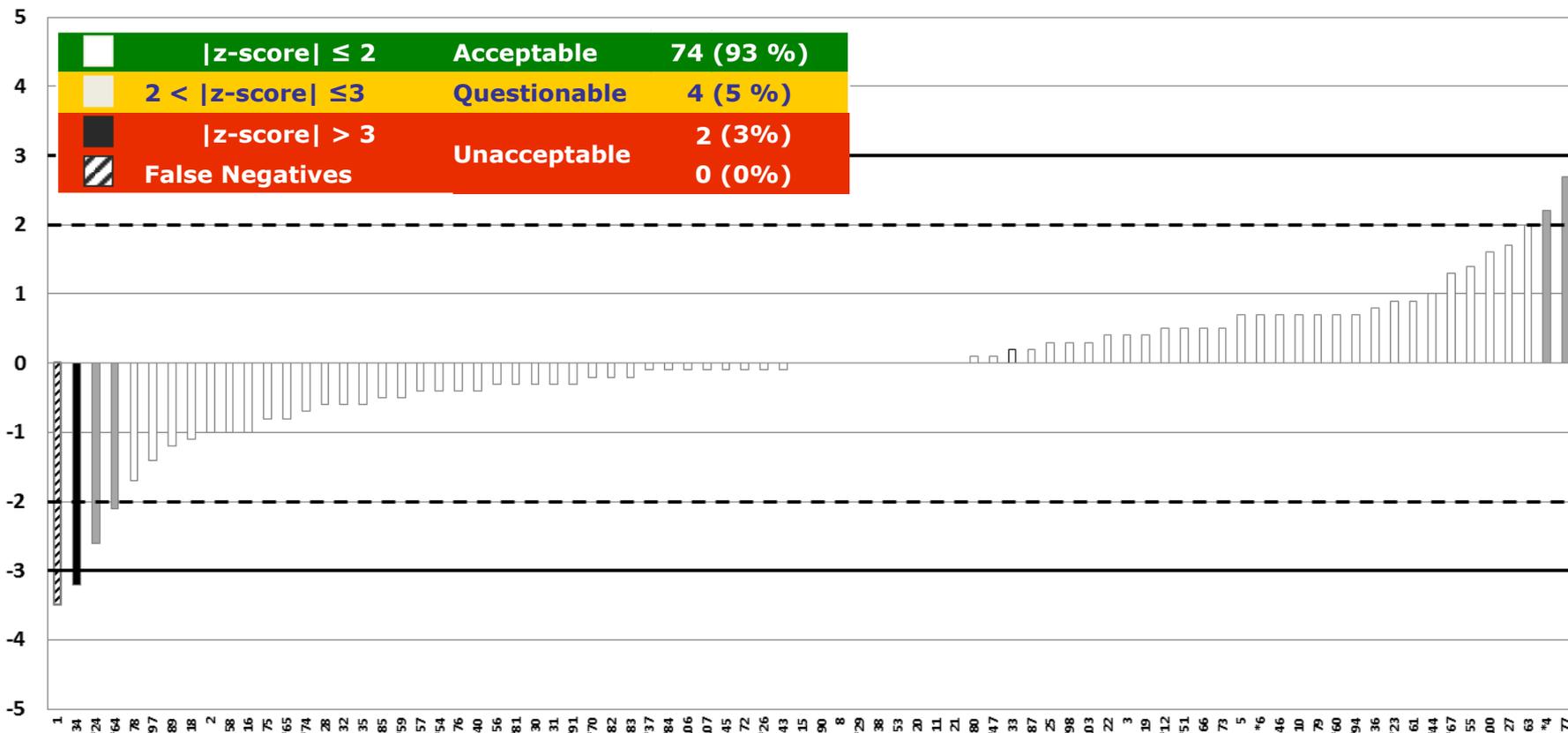
Bimodality ?  
EUPT-AdvG: No action needed

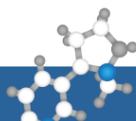




# MCPA

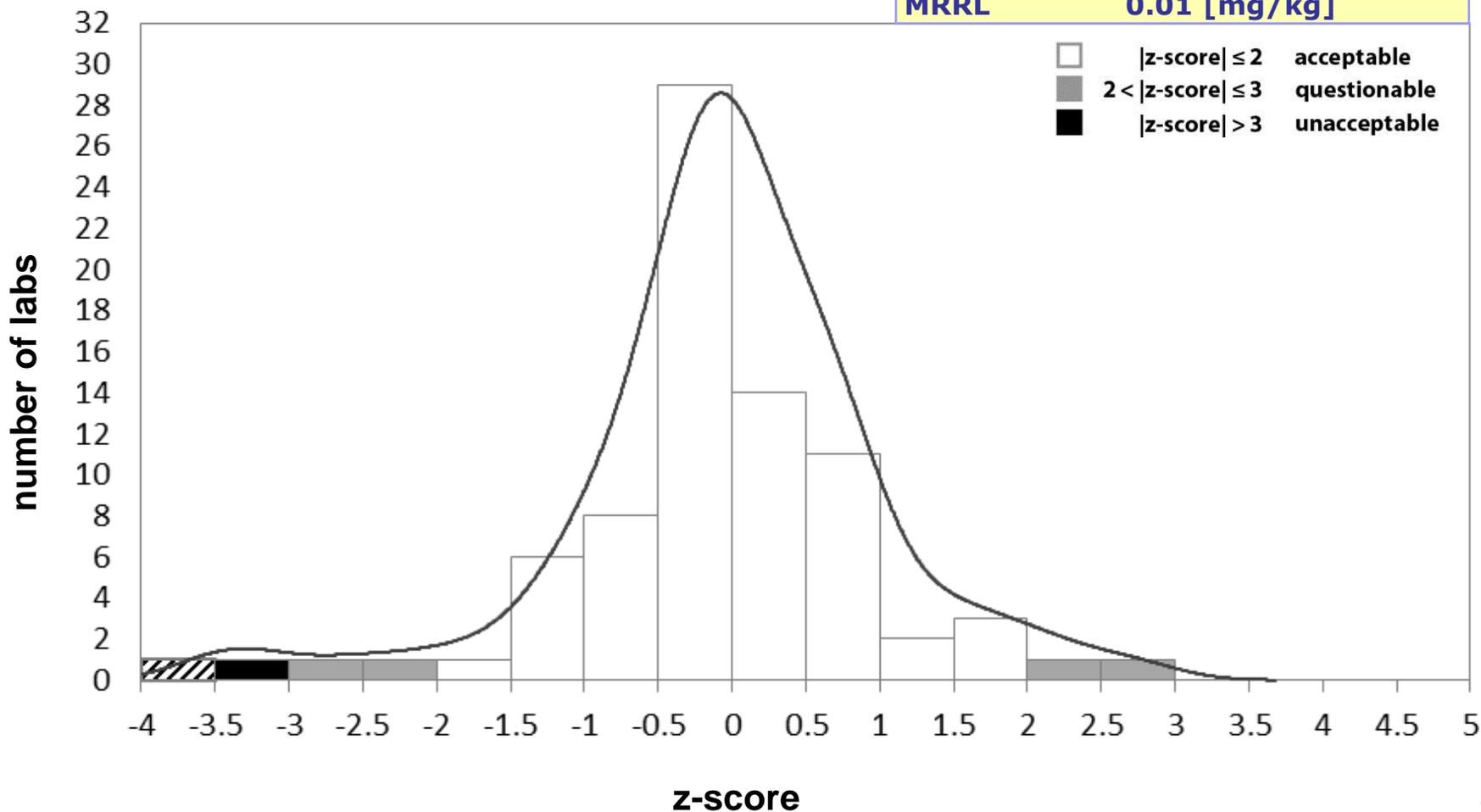
|                    |                      |
|--------------------|----------------------|
| <b>Results</b>     | <b>80</b>            |
| <b>False Neg.</b>  | <b>0</b>             |
| <b>Robust Mean</b> | <b>0.081 [mg/kg]</b> |
| <b>Robust RSD</b>  | <b>18.9 %</b>        |
| <b>MRRL</b>        | <b>0.01 [mg/kg]</b>  |

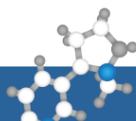




|                    |                      |
|--------------------|----------------------|
| <b>Results</b>     | <b>80</b>            |
| <b>False Neg.</b>  | <b>0</b>             |
| <b>Robust Mean</b> | <b>0.081 [mg/kg]</b> |
| <b>Robust RSD</b>  | <b>18.9 %</b>        |
| <b>MRRL</b>        | <b>0.01 [mg/kg]</b>  |

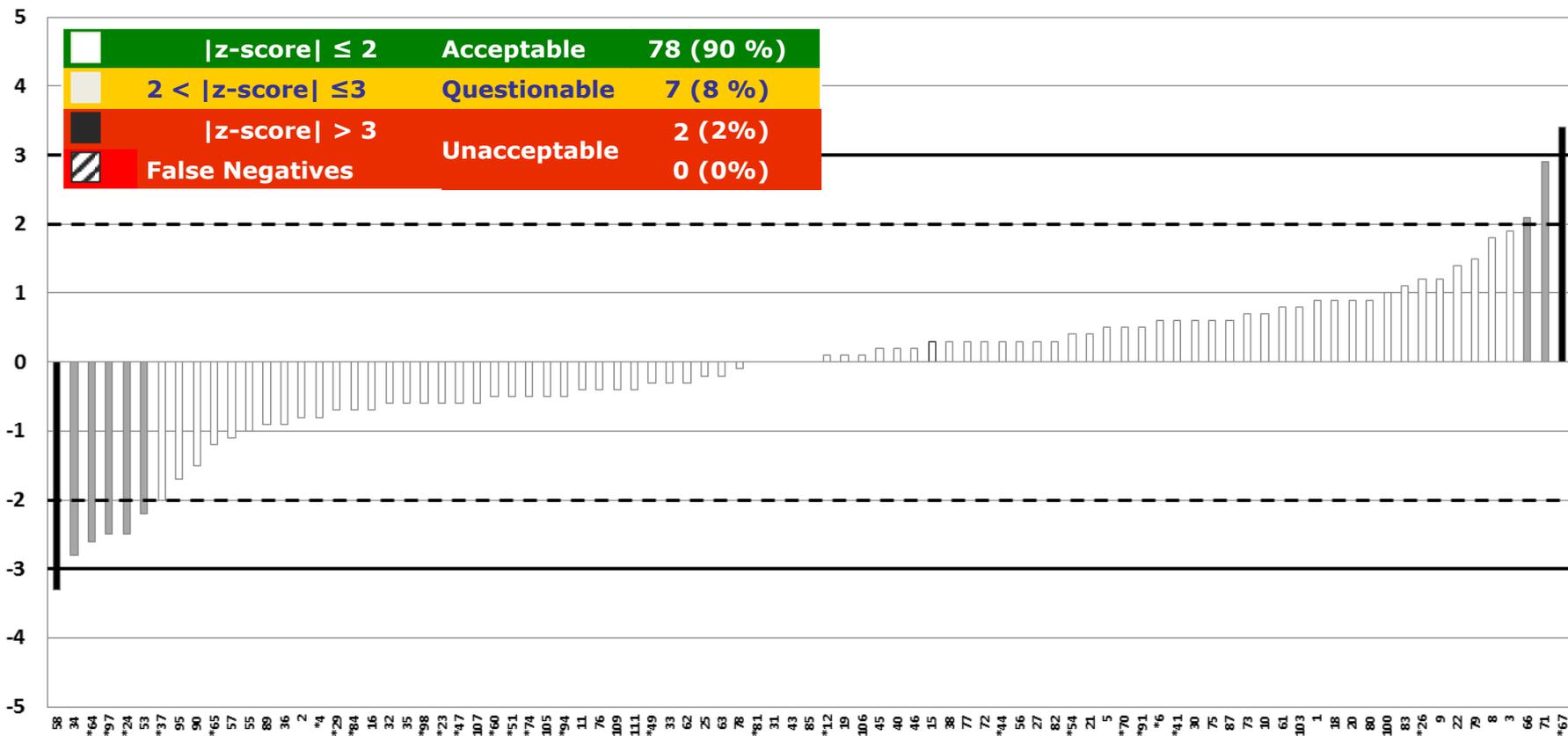
# MCPA

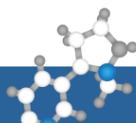




# PROPAMOCARB

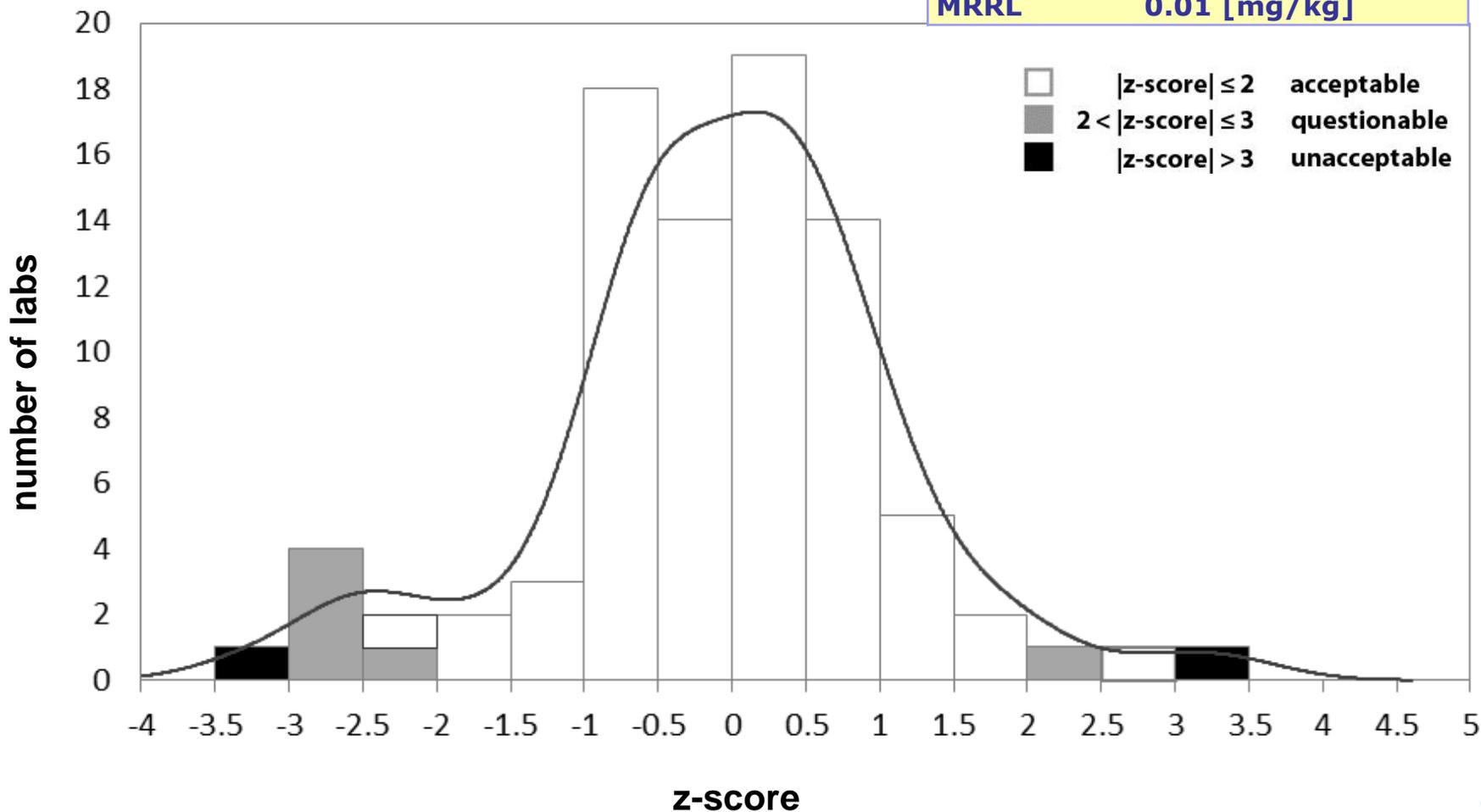
|                    |                      |
|--------------------|----------------------|
| <b>Results</b>     | <b>87</b>            |
| <b>False Neg.</b>  | <b>0</b>             |
| <b>Robust Mean</b> | <b>0.067 [mg/kg]</b> |
| <b>Robust RSD</b>  | <b>23.3 %</b>        |
| <b>MRRL</b>        | <b>0.01 [mg/kg]</b>  |

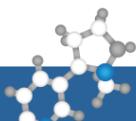




# PROPAMOCARB

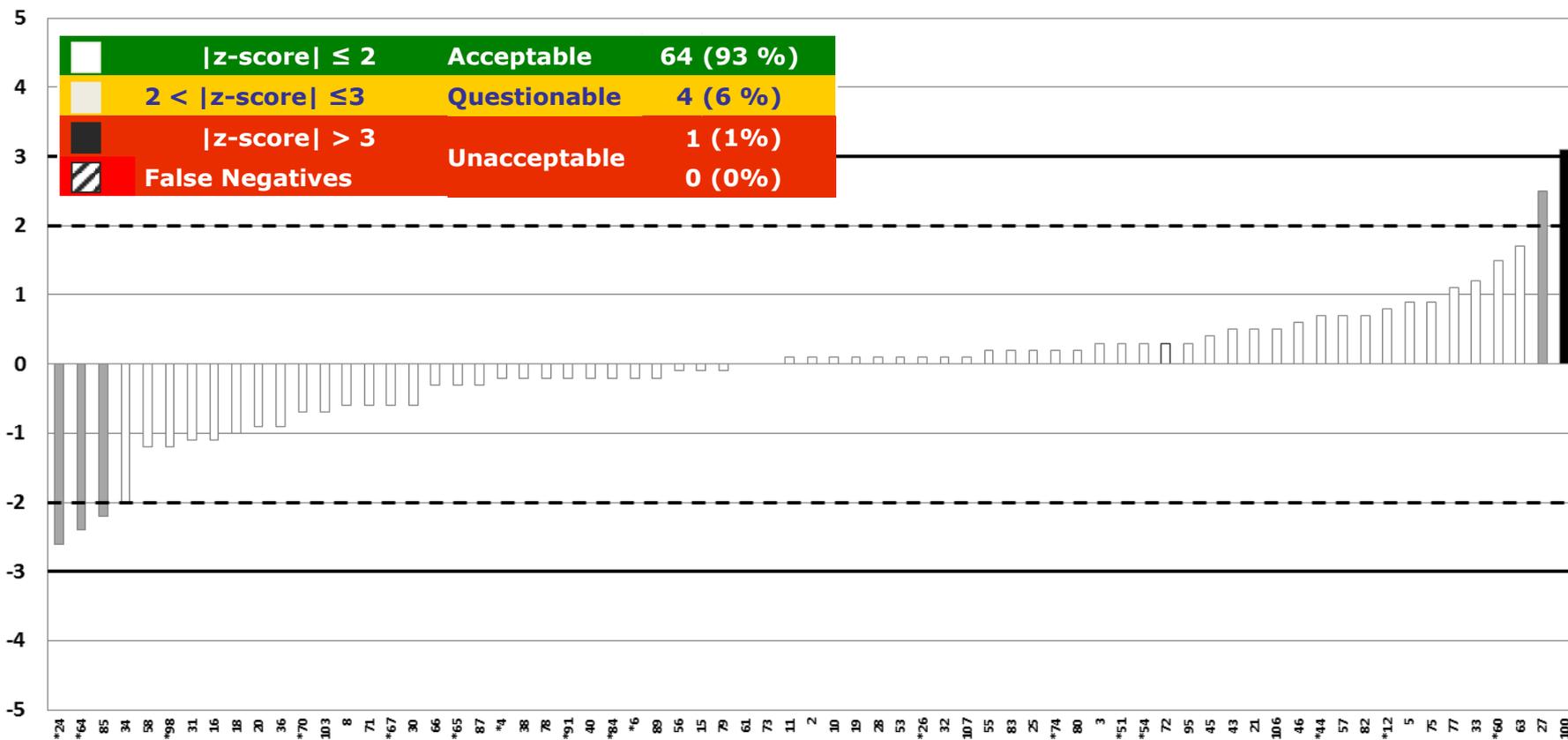
|             |               |
|-------------|---------------|
| Results     | 87            |
| False Neg.  | 0             |
| Robust Mean | 0.067 [mg/kg] |
| Robust RSD  | 23.3 %        |
| MRRL        | 0.01 [mg/kg]  |

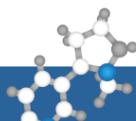




# BENTAZONE

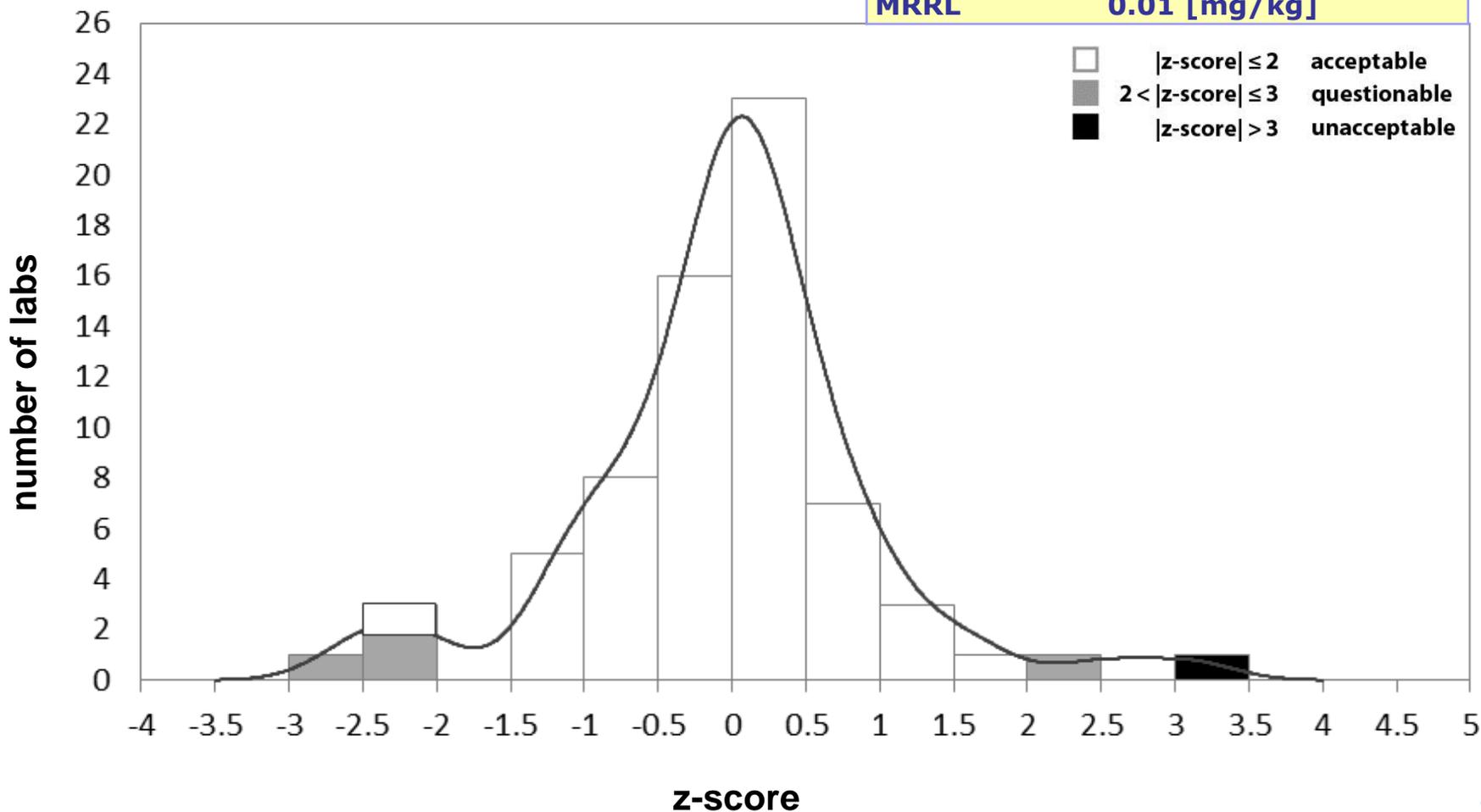
|                    |                      |
|--------------------|----------------------|
| <b>Results</b>     | <b>69</b>            |
| <b>False Neg.</b>  | <b>0</b>             |
| <b>Robust Mean</b> | <b>0.098 [mg/kg]</b> |
| <b>Robust RSD</b>  | <b>18.5 %</b>        |
| <b>MRRL</b>        | <b>0.01 [mg/kg]</b>  |

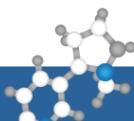




|                    |                      |
|--------------------|----------------------|
| <b>Results</b>     | <b>69</b>            |
| <b>False Neg.</b>  | <b>0</b>             |
| <b>Robust Mean</b> | <b>0.098 [mg/kg]</b> |
| <b>Robust RSD</b>  | <b>18.5 %</b>        |
| <b>MRRL</b>        | <b>0.01 [mg/kg]</b>  |

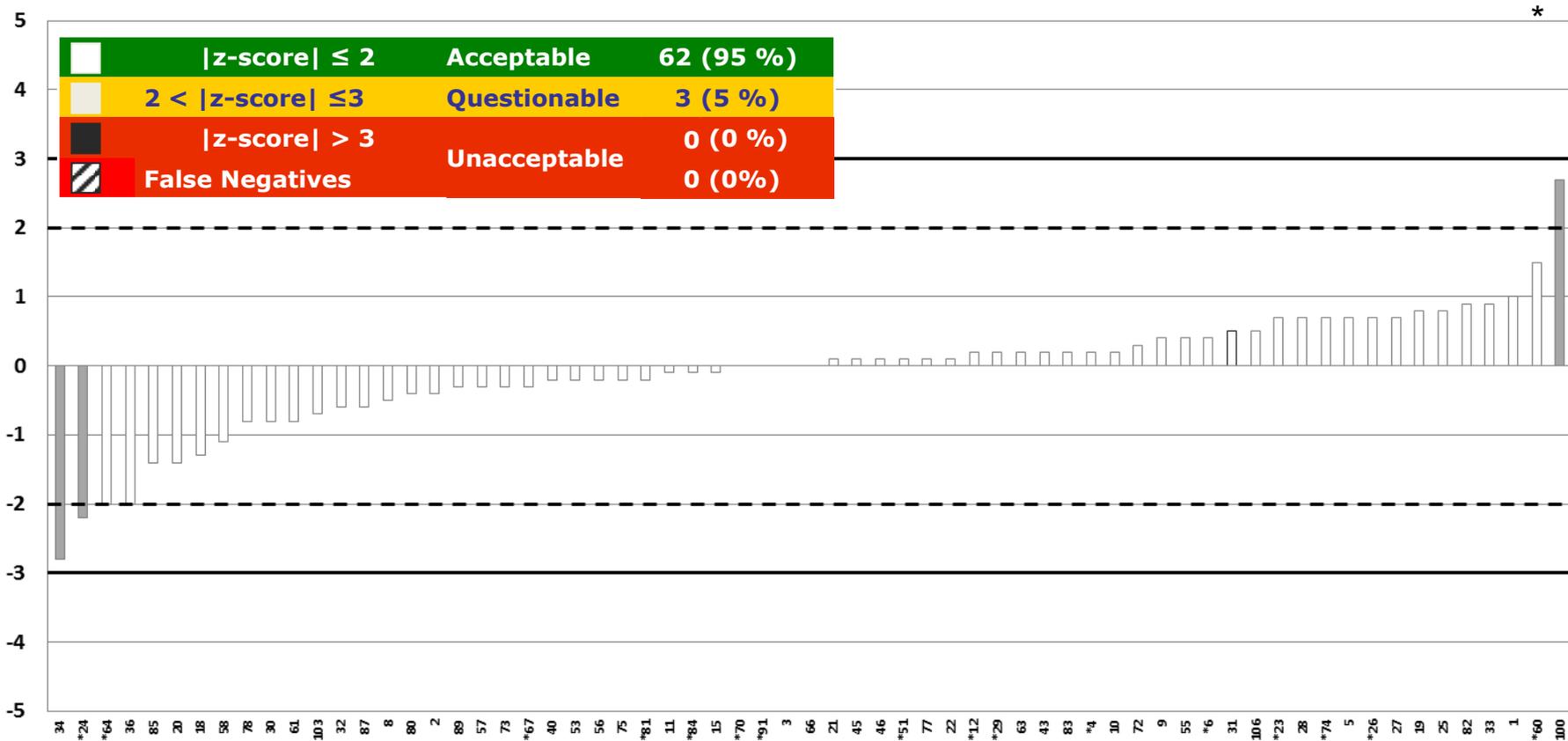
# BENTAZONE

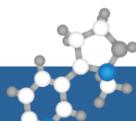




# BROMOXYNIL

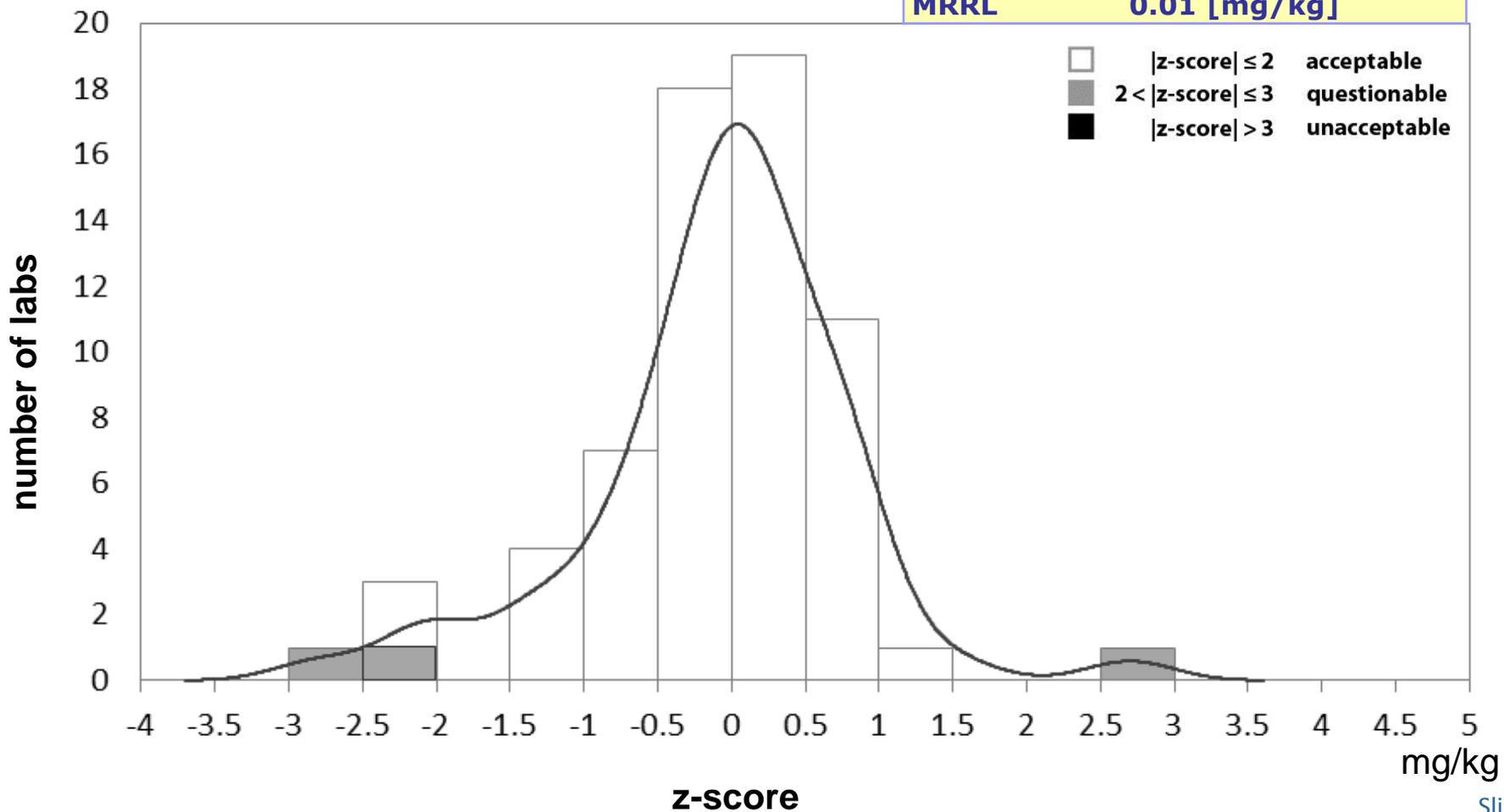
|                    |                      |
|--------------------|----------------------|
| <b>Results</b>     | <b>65</b>            |
| <b>False Neg.</b>  | <b>0</b>             |
| <b>Robust Mean</b> | <b>0.125 [mg/kg]</b> |
| <b>Robust RSD</b>  | <b>17.0 %</b>        |
| <b>MRRL</b>        | <b>0.01 [mg/kg]</b>  |

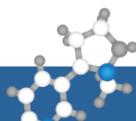




|                    |                      |
|--------------------|----------------------|
| <b>Results</b>     | <b>65</b>            |
| <b>False Neg.</b>  | <b>0</b>             |
| <b>Robust Mean</b> | <b>0.125 [mg/kg]</b> |
| <b>Robust RSD</b>  | <b>17.0 %</b>        |
| <b>MRRL</b>        | <b>0.01 [mg/kg]</b>  |

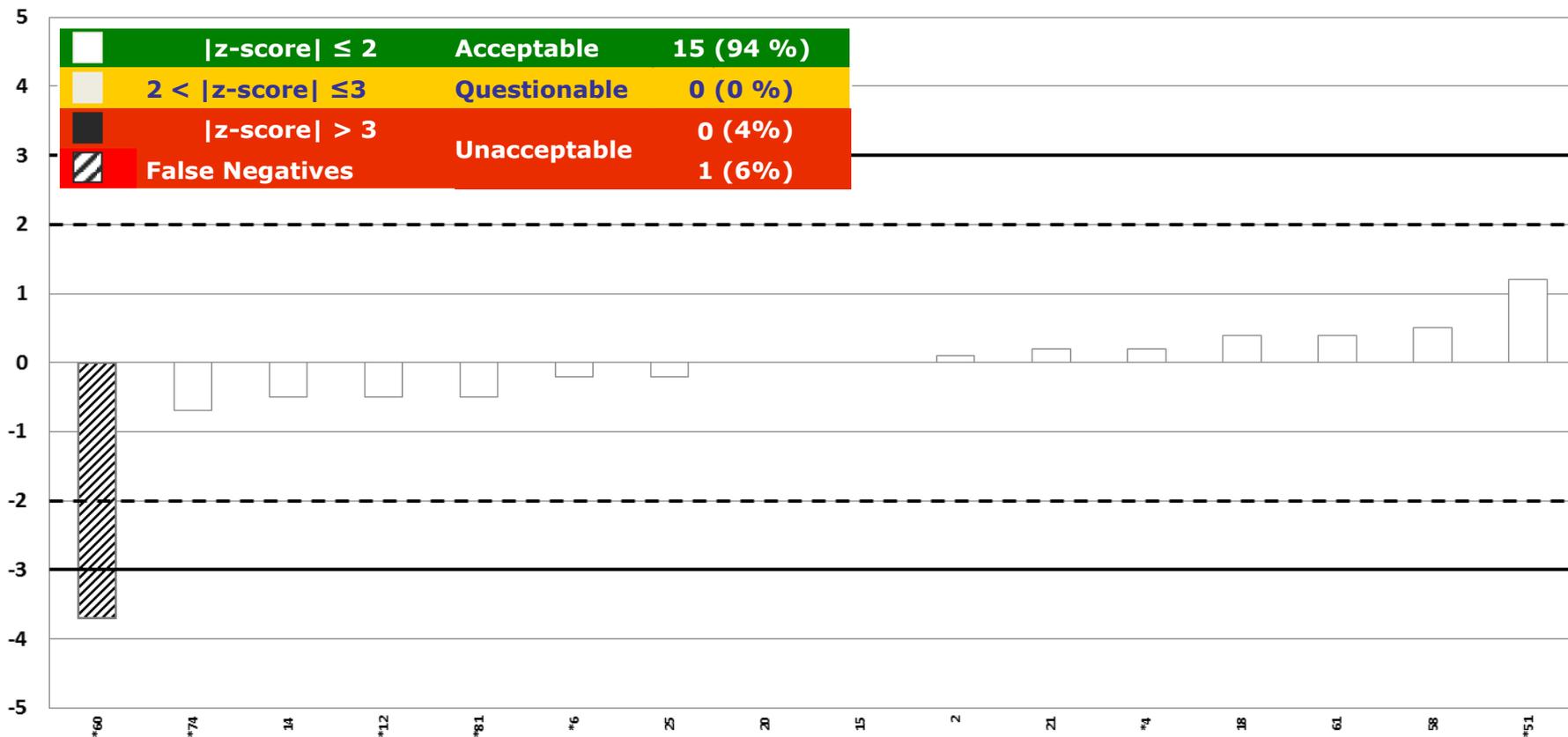
# BROMOXYNIL

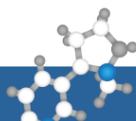




# N-ACETYL GLUFOSINATE

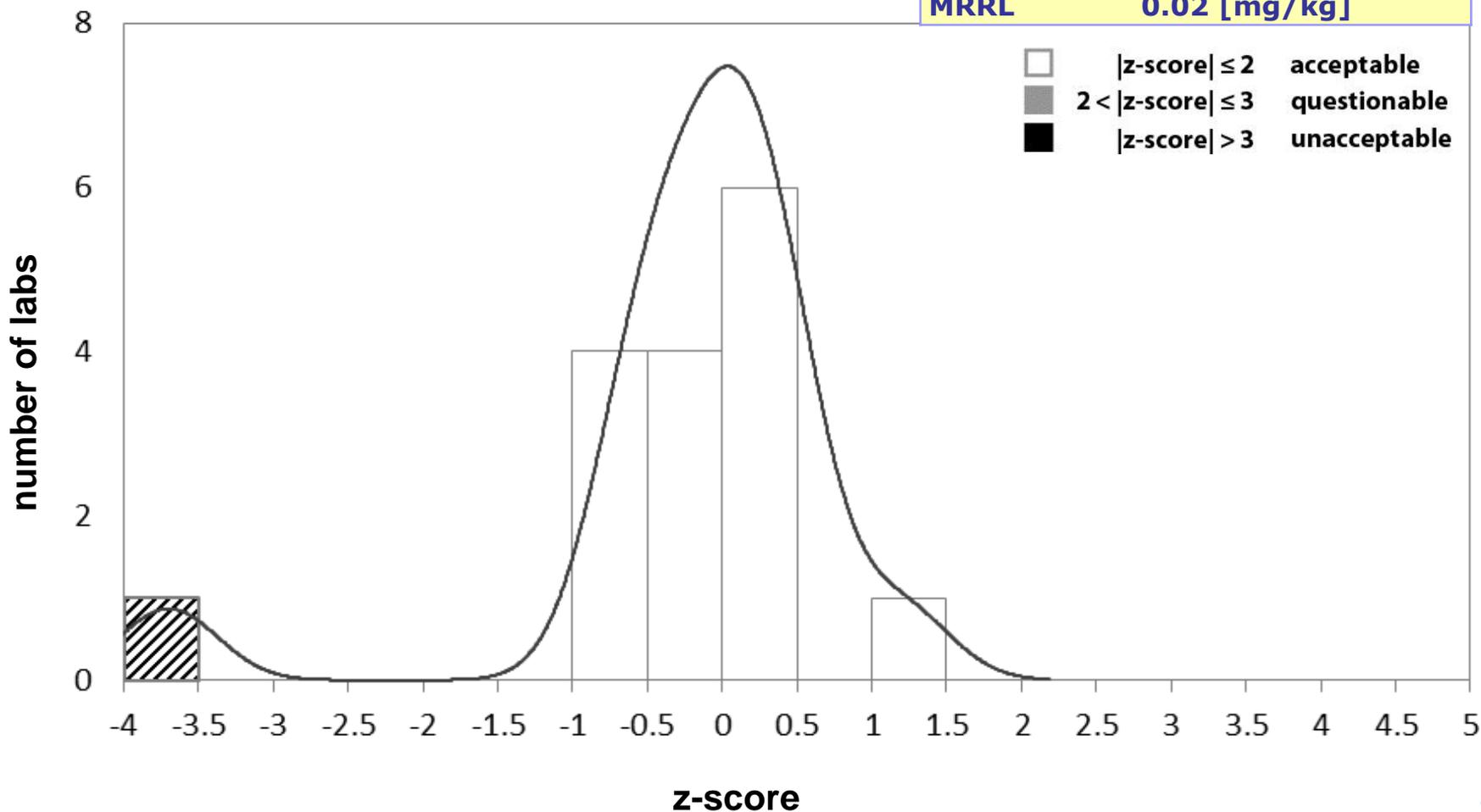
|                    |                      |
|--------------------|----------------------|
| <b>Results</b>     | <b>15</b>            |
| <b>False Neg.</b>  | <b>1</b>             |
| <b>Robust Mean</b> | <b>0.319 [mg/kg]</b> |
| <b>Robust RSD</b>  | <b>11.8 %</b>        |
| <b>MRRL</b>        | <b>0.02 [mg/kg]</b>  |

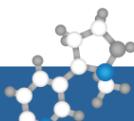




|                    |                      |
|--------------------|----------------------|
| <b>Results</b>     | <b>15</b>            |
| <b>False Neg.</b>  | <b>1</b>             |
| <b>Robust Mean</b> | <b>0.319 [mg/kg]</b> |
| <b>Robust RSD</b>  | <b>11.8 %</b>        |
| <b>MRRL</b>        | <b>0.02 [mg/kg]</b>  |

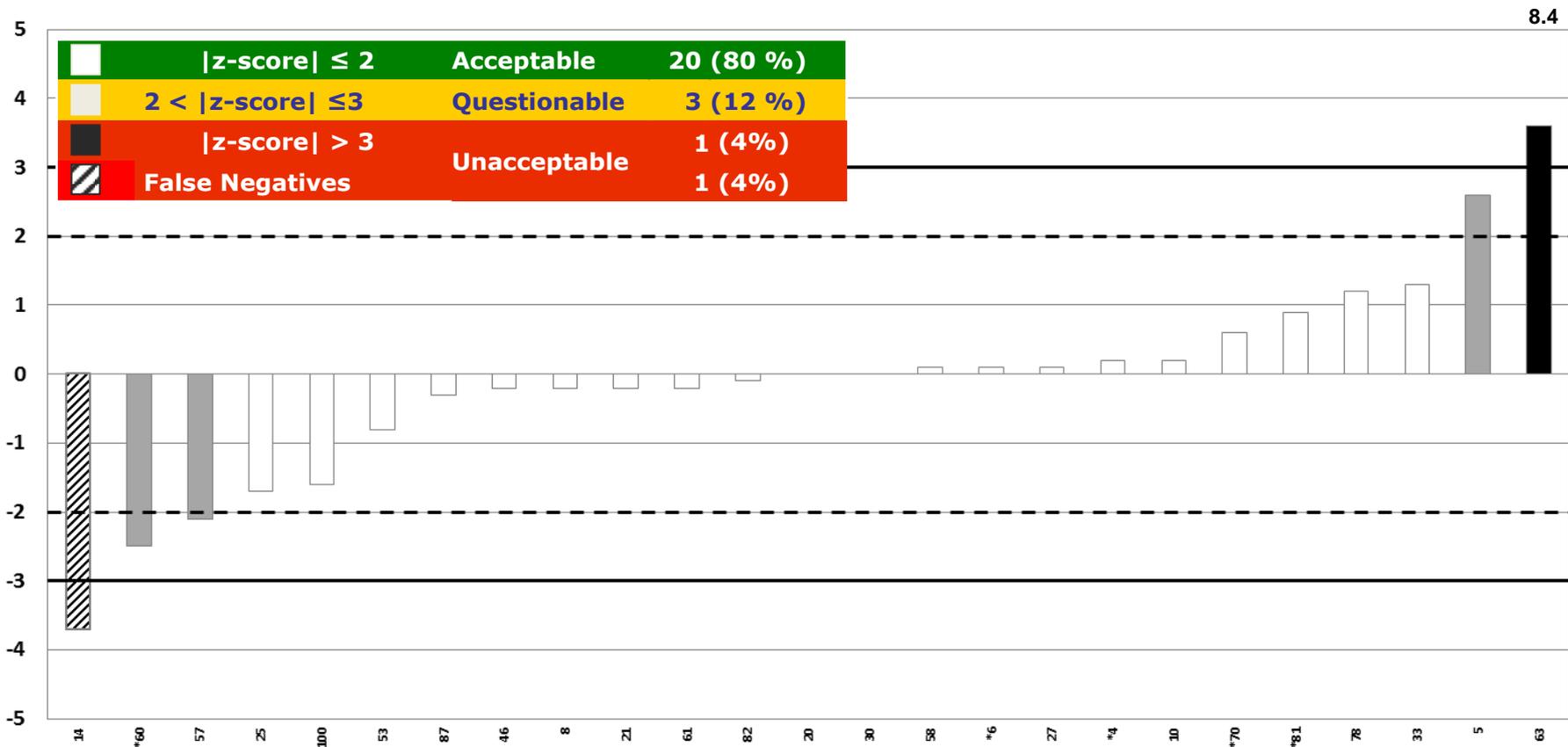
# N-ACETYL GLUFOSINATE

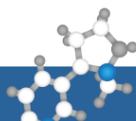




# PHOSPHONIC ACID

|            |               |
|------------|---------------|
| Results    | 24            |
| False Neg. | 1             |
| Median     | 0.584 [mg/kg] |
| Robust RSD | 27.3 %        |
| MRRL       | 0.05 [mg/kg]  |

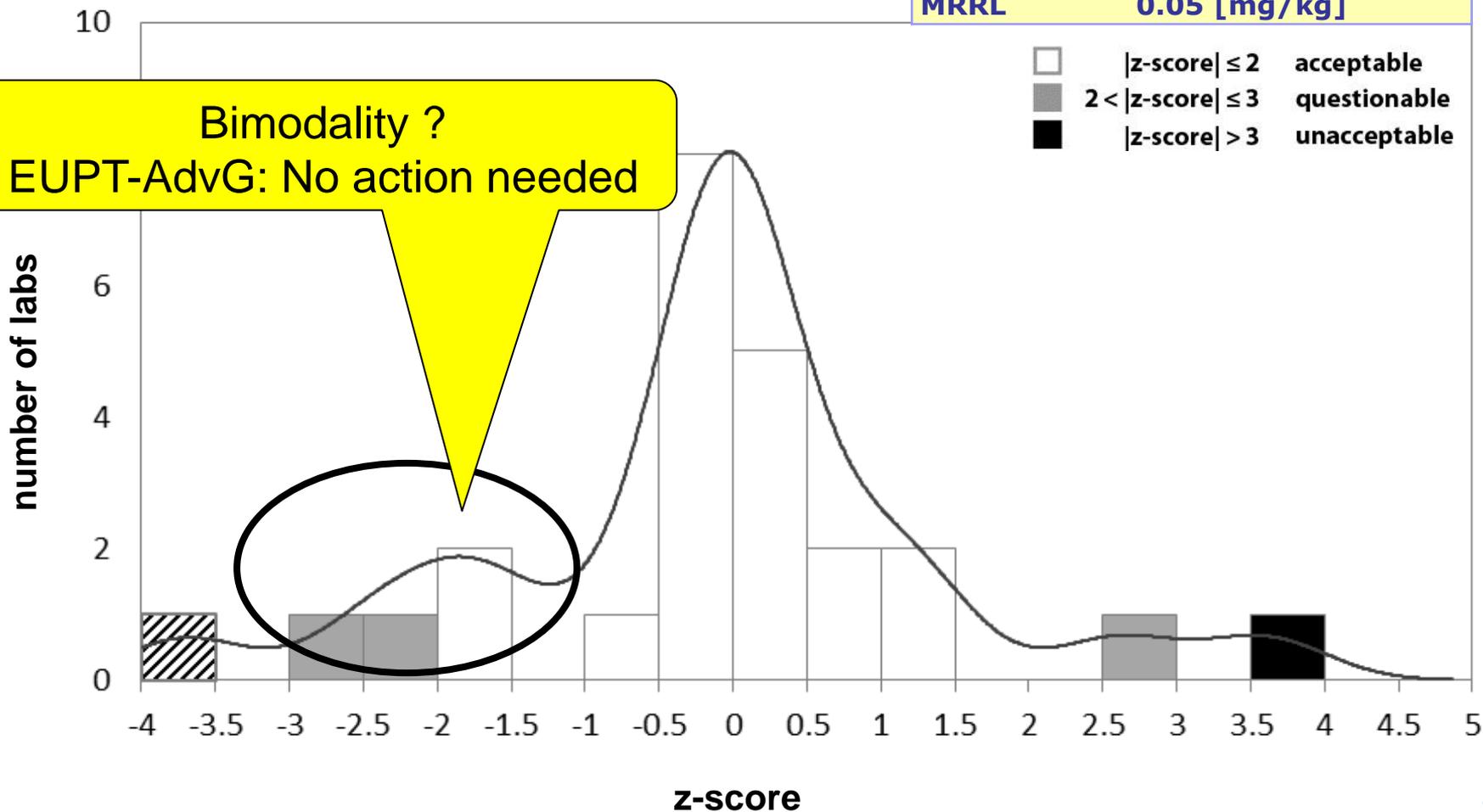


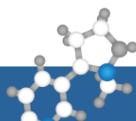


# PHOSPHONIC ACID

|                   |                      |
|-------------------|----------------------|
| <b>Results</b>    | <b>24</b>            |
| <b>False Neg.</b> | <b>1</b>             |
| <b>Median</b>     | <b>0.584 [mg/kg]</b> |
| <b>Robust RSD</b> | <b>27.3 %</b>        |
| <b>MRRL</b>       | <b>0.05 [mg/kg]</b>  |

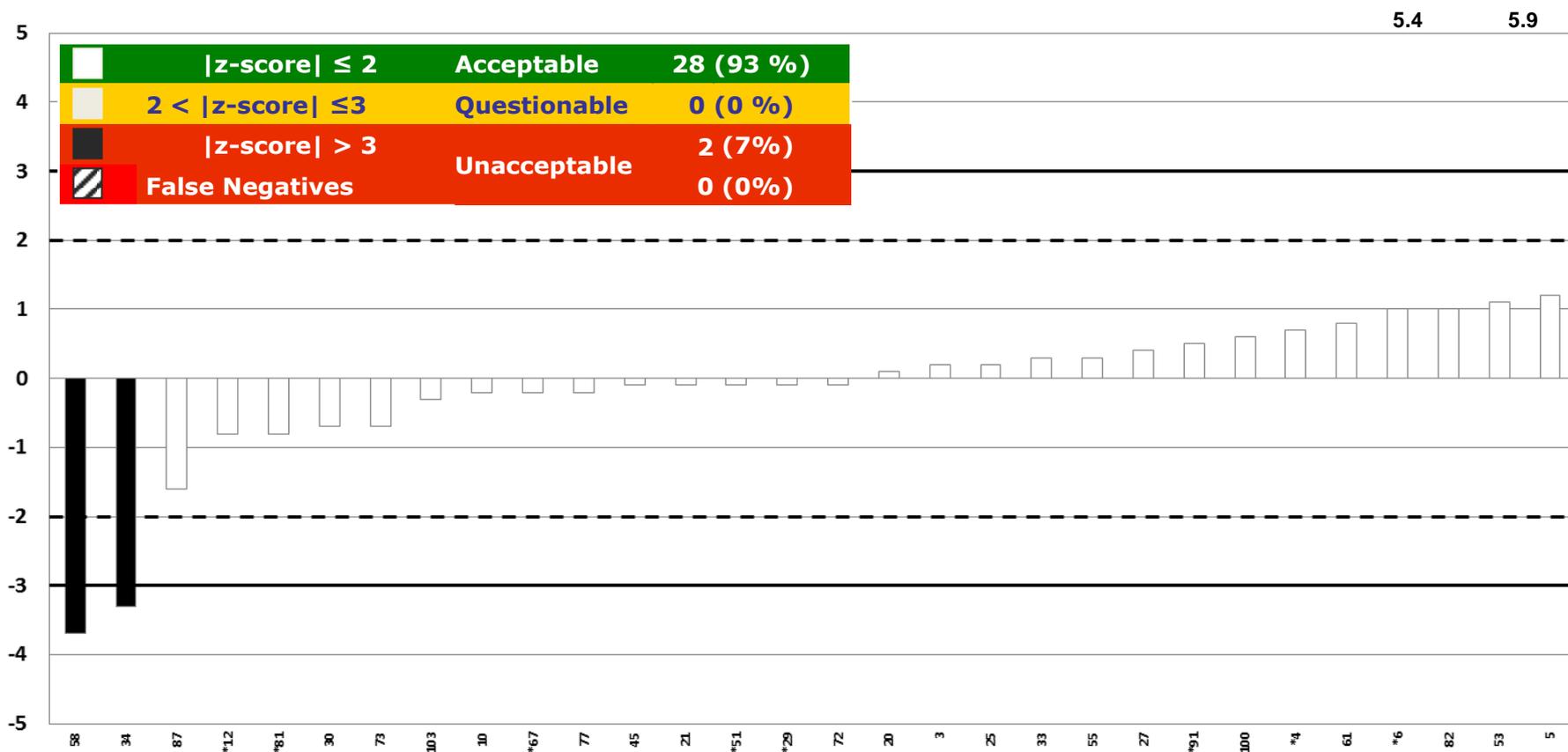
Bimodality ?  
EUPT-AdvG: No action needed





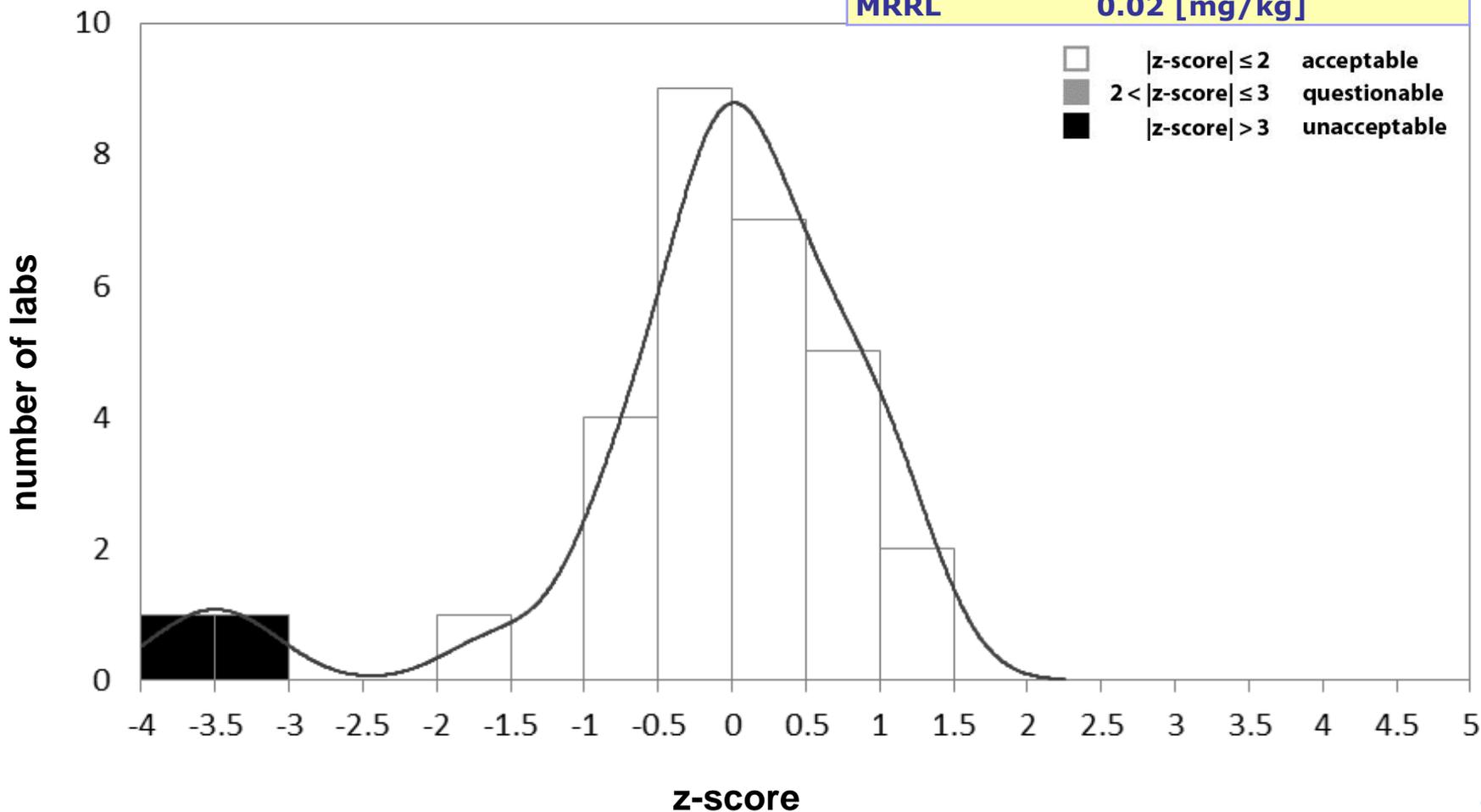
# TFNG

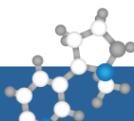
|                    |                      |
|--------------------|----------------------|
| <b>Results</b>     | <b>30</b>            |
| <b>False Neg.</b>  | <b>0</b>             |
| <b>Robust Mean</b> | <b>0.168 [mg/kg]</b> |
| <b>Robust RSD</b>  | <b>18.6 %</b>        |
| <b>MRRL</b>        | <b>0.02 [mg/kg]</b>  |



|                    |                      |
|--------------------|----------------------|
| <b>Results</b>     | <b>30</b>            |
| <b>False Neg.</b>  | <b>0</b>             |
| <b>Robust Mean</b> | <b>0.168 [mg/kg]</b> |
| <b>Robust RSD</b>  | <b>18.6 %</b>        |
| <b>MRRL</b>        | <b>0.02 [mg/kg]</b>  |

# TFNG

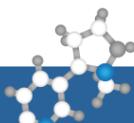




# UNCERTAINTY OF ASSIGNED VALUE

## Compulsory Compounds

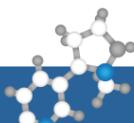
| Compound         | No. of Numerical Results | Robust-RSD [%] | Assigned Value (AV, Robust Mean) [mg/kg] | Uncertainty of Robust Mean (AV) [mg/kg] | UAV Tolerance [mg/kg] | Judgement |
|------------------|--------------------------|----------------|------------------------------------------|-----------------------------------------|-----------------------|-----------|
| 2,4-D            | 82                       | 18.2           | 0.092                                    | +/- 0.00232                             | 0.0069                | passed    |
| Chlormequat      | 75                       | 18.2           | 0.167                                    | +/- 0.00440                             | 0.0126                | passed    |
| Dithiocarbamates | 85                       | 36.9           | 0.559                                    | +/- 0.02800                             | 0.0419                | passed    |
| Ethephon         | 61                       | 30.8           | 0.162                                    | +/- 0.00797                             | 0.0121                | passed    |
| Glyphosate       | 62                       | 22.8           | 0.568                                    | +/- 0.02059                             | 0.0426                | passed    |
| MCPA             | 79                       | 18.9           | 0.081                                    | +/- 0.00215                             | 0.0061                | passed    |
| Mepiquat         | 76                       | 18.5           | 0.114                                    | +/- 0.00302                             | 0.0085                | passed    |
| Propamocarb      | 87                       | 23.3           | 0.067                                    | +/- 0.00208                             | 0.0050                | passed    |



# UNCERTAINTY OF ASSIGNED VALUE

## Optional Compounds

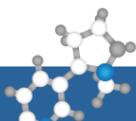
| <b>Compound</b>             | <b>No. of Numerical Results</b> | <b>Robust-RSD [%]</b> | <b>Assigned Value (AV, Robust Mean) [mg/kg]</b> | <b>Uncertainty of Robust Mean (UAV) [mg/kg]</b> | <b>UAV-Tolerance [mg/kg]</b> | <b>Judgement</b> |
|-----------------------------|---------------------------------|-----------------------|-------------------------------------------------|-------------------------------------------------|------------------------------|------------------|
| <b>Bentazone</b>            | <b>69</b>                       | <b>18.5</b>           | <b>0.098</b>                                    | <b>0.00272</b>                                  | <b>0.0073</b>                | <b>passed</b>    |
| <b>Bromoxynil</b>           | <b>65</b>                       | <b>17.0</b>           | <b>0.125</b>                                    | <b>0.00329</b>                                  | <b>0.0094</b>                | <b>passed</b>    |
| <b>N-Acetyl Glufosinate</b> | <b>15</b>                       | <b>11.8</b>           | <b>0.319</b>                                    | <b>0.01211</b>                                  | <b>0.0293</b>                | <b>passed</b>    |
| <b>Phosphonic acid</b>      | <b>24</b>                       | <b>27.3</b>           | <b>0.584</b>                                    | <b>0.04064</b>                                  | <b>0.0438</b>                | <b>passed</b>    |
| <b>TFNG</b>                 | <b>30</b>                       | <b>18.6</b>           | <b>0.168</b>                                    | <b>0.00712</b>                                  | <b>0.0126</b>                | <b>passed</b>    |



EU+EFTA

Compulsory compounds:

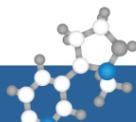
| Compound         | No. of Labs | FNs | AAZ  | Robust-RSD [%] | <br>A | <br>Q | <br>U |
|------------------|-------------|-----|------|----------------|------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|
| 2,4-D            | 82          | 0   | 0.65 | 18.2           | 96 %                                                                                     | 2 %                                                                                      | 1 %                                                                                      |
| Chlormequat      | 75          | 0   | 0.73 | 18.2           | 91 %                                                                                     | 7 %                                                                                      | 3 %                                                                                      |
| Dithiocarbamates | 86          | 1   | 1.18 | 36.9           | 78 %                                                                                     | 15 %                                                                                     | 7 %                                                                                      |
| Ethephon         | 61          | 0   | 1.11 | 30.8           | 85 %                                                                                     | 8 %                                                                                      | 7 %                                                                                      |
| Glyphosate       | 64          | 2   | 0.89 | 22.8           | 88 %                                                                                     | 8 %                                                                                      | 5 %                                                                                      |
| MCPA             | 80          | 1   | 0.69 | 18.9           | 93 %                                                                                     | 5 %                                                                                      | 3 %                                                                                      |
| Mepiquat         | 76          | 0   | 0.74 | 18.5           | 91 %                                                                                     | 4 %                                                                                      | 5 %                                                                                      |
| Propamocarb      | 87          | 0   | 0.85 | 23.3           | 90 %                                                                                     | 8 %                                                                                      | 2 %                                                                                      |



EU+EFTA

# Optional Compounds:

| Compound             | No. of Labs | FNs | AAZ  | Qn-RSD [%] | <br>A | <br>Q | <br>U |
|----------------------|-------------|-----|------|------------|------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|
| Bentazone            | 69          | 0   | 0.65 | 18.5       | 93 %                                                                                     | 6 %                                                                                      | 1 %                                                                                      |
| Bromoxynil           | 65          | 0   | 0.61 | 17.0       | 95 %                                                                                     | 5 %                                                                                      | 0 %                                                                                      |
| N-Acetyl Glufosinate | 16          | 1   | 0.58 | 11.8       | 94 %                                                                                     | 0 %                                                                                      | 6 %                                                                                      |
| Phosphonic acid      | 25          | 1   | 0.98 | 27.3       | 80 %                                                                                     | 12 %                                                                                     | 8 %                                                                                      |
| TFNG                 | 30          | 0   | 0.71 | 18.6       | 93 %                                                                                     | 0 %                                                                                      | 7 %                                                                                      |



## Rules for Category A:

**EU+EFTA**

- Numerical results for at least 7 out of 8 compulsory pesticides present in test item
- No FPs

|                   | <b>No. of Labs</b> | <b>[%]</b> |
|-------------------|--------------------|------------|
| <b>Category A</b> | 44                 | 42 %       |
| <b>Category B</b> | 60                 | 58 %       |

|                   |           |     |
|-------------------|-----------|-----|
| <b>2,4-D</b>      | <b>89</b> |     |
| QuEChERS          | 72        | 81% |
| Other             | 9         | 10% |
| SweEt             | 2         | 2%  |
| QuPPE             | 2         | 2%  |
| MiniLuke          | 2         | 2%  |
| ChemElut          | 2         | 2%  |
| <b>Bentazone</b>  | <b>76</b> |     |
| QuEChERS          | 63        | 83% |
| Other             | 7         | 9%  |
| QuPPE             | 2         | 3%  |
| MiniLuke          | 2         | 3%  |
| SweEt             | 1         | 1%  |
| ChemElut          | 1         | 1%  |
| <b>Bromoxynil</b> | <b>71</b> |     |
| QuEChERS          | 57        | 80% |
| Other             | 7         | 10% |
| MiniLuke          | 2         | 3%  |
| QuPPE             | 2         | 3%  |
| ChemElut          | 2         | 3%  |
| SweEt             | 1         | 1%  |

## METHODS USED - ACIDIC COMPOUNDS -

|             |           |     |
|-------------|-----------|-----|
| <b>MCPA</b> | <b>86</b> |     |
| QuEChERS    | 70        | 81% |
| Other       | 9         | 10% |
| SweEt       | 2         | 2%  |
| QuPPE       | 2         | 2%  |
| MiniLuke    | 2         | 2%  |
| ChemElut    | 1         | 1%  |
| <b>TFNG</b> | <b>33</b> |     |
| QuEChERS    | 31        | 94% |
| QuPPE       | 1         | 3%  |
| MiniLuke    | 1         | 3%  |

|                    |           |     |
|--------------------|-----------|-----|
| <b>Chlormequat</b> | <b>80</b> |     |
| QuPpe              | 53        | 66% |
| Other              | 18        | 23% |
| QuEChERS           | 7         | 9%  |
| ChemElut           | 1         | 1%  |
| <b>Ethephon</b>    | <b>67</b> |     |
| QuPpe              | 52        | 78% |
| Other              | 8         | 12% |
| QuEChERS           | 5         | 7%  |
| Ethylene-basis     | 2         | 3%  |
| <b>Glyphosate</b>  | <b>70</b> |     |
| QuPpe              | 38        | 54% |
| Gly-FMOC           | 21        | 30% |
| Other              | 6         | 9%  |
| QuEChERS           | 3         | 4%  |
| Gly-OPA            | 2         | 3%  |
| <b>Mepiquat</b>    | <b>80</b> |     |
| QuPpe              | 53        | 66% |
| Other              | 18        | 23% |
| QuEChERS           | 8         | 10% |
| ChemElut           | 1         | 1%  |

## METHODS USED - POLAR COMPOUNDS -

|                      |           |     |
|----------------------|-----------|-----|
| <b>NAG</b>           | <b>16</b> |     |
| QuPpe                | 15        | 94% |
| Other                | 1         | 6%  |
| <b>Phosphonic A.</b> | <b>26</b> |     |
| QuPpe                | 22        | 85% |
| Other                | 2         | 8%  |
| QuEChERS             | 2         | 8%  |
| <b>Propamocarb</b>   | <b>92</b> |     |
| QuEChERS             | 69        | 75% |
| QuPpe                | 10        | 11% |
| Other                | 7         | 8%  |
| SweEt                | 3         | 3%  |
| ChemElut             | 2         | 2%  |
| MiniLuke             | 1         | 1%  |

# METHODS USED - DITHIOCARBAMATES -

| <b>Dithiocarbamates</b> | <b>92</b> | <b>%</b> |
|-------------------------|-----------|----------|
| DTC-Isooctane           | 35        | 38%      |
| DTC-Head Space          | 24        | 26%      |
| DTC-Xanthogenate        | 14        | 15%      |
| DTC-Cu-Acetate          | 8         | 9%       |
| Other                   | 5         | 5%       |
| DTC-SPME                | 5         | 5%       |
| „QuEChERS“              | 1         | 1%       |

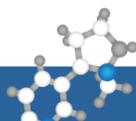


# Use of isotope labelled ISTDs

**EU+EFTA**

| Compulsory Compound | No. of Labs | Using IL-IS | %   |
|---------------------|-------------|-------------|-----|
| 2,4-D               | 82          | 6           | 7%  |
| Chlormequat         | 75          | 45          | 60% |
| Dithiocarbamates    | 86          | 3           | 3%  |
| Ethephon            | 61          | 31          | 51% |
| Glyphosate          | 64          | 43          | 67% |
| MCPA                | 80          | 7           | 9%  |
| Mepiquat            | 76          | 44          | 58% |
| Propamocarb         | 87          | 9           | 10% |

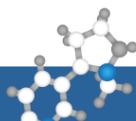
| Optional Compound    | No. of Labs | Using IL-IS | %   |
|----------------------|-------------|-------------|-----|
| Bentazone            | 69          | 7           | 10% |
| Bromoxynil           | 65          | 4           | 6%  |
| N-Acetyl Glufosinate | 16          | 7           | 44% |
| Phosphonic acid      | 25          | 18          | 72% |
| TFNG                 | 30          | 1           | 3%  |



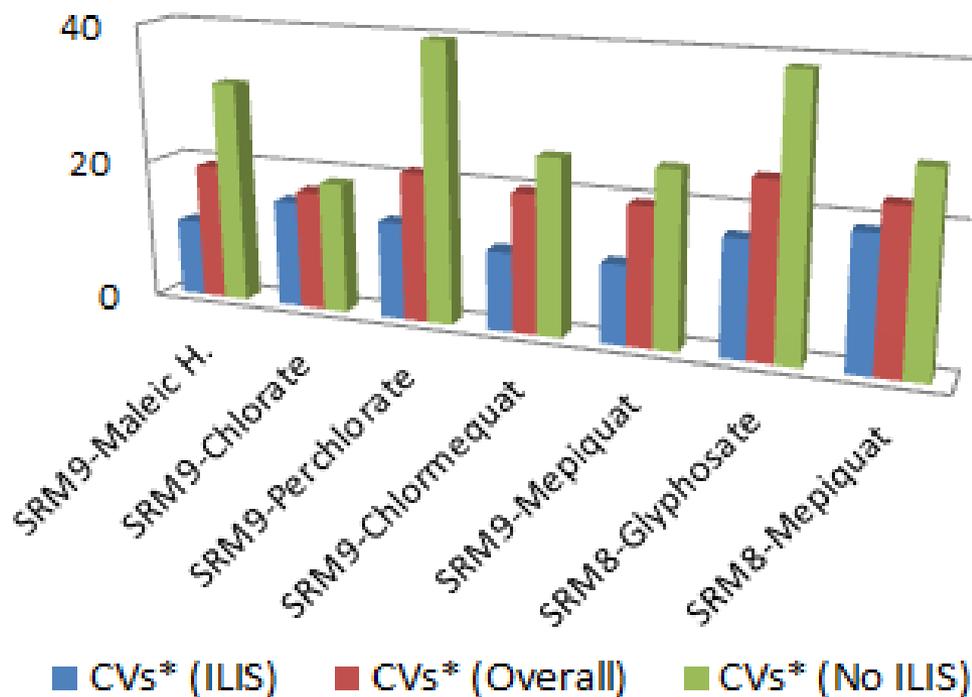
**EU+EFTA**

# Impact of IL-IS on Qn-RSD and FNs

| Compound          | OVERALL     |                   |      | WITH IL-IS |                   |      |     | W/O IL-IS |                   |      |     |
|-------------------|-------------|-------------------|------|------------|-------------------|------|-----|-----------|-------------------|------|-----|
|                   | No. of Labs | CV <sub>s</sub> * | AAZ  | %          | CV <sub>s</sub> * | AAZ  | FNs | %         | CV <sub>s</sub> * | AAZ  | FNs |
| <b>COMPULSORY</b> |             |                   |      |            |                   |      |     |           |                   |      |     |
| Chlormequat       | 75          | 18.2%             | 0.73 | 60%        | 15%               | 0.70 | –   | 40%       | 24%               | 1.02 | –   |
| Ethephon          | 61          | 30.8%             | 1.11 | 51%        | 29%               | 1.11 | –   | 49%       | 31%               | 1.36 | –   |
| Glyphosate        | 64          | 22.8%             | 0.89 | 67%        | 17%               | 0.55 | –   | 33%       | 42%               | 0.60 | 2   |
| Mepiquat          | 76          | 18.5%             | 0.74 | 58%        | 21%               | 0.85 | –   | 42%       | 16%               | 0.77 | –   |
|                   |             |                   |      | AVG.       | 21%               | 0,80 |     |           | 28%               | 0,94 |     |
| <b>OPTIONAL</b>   |             |                   |      |            |                   |      |     |           |                   |      |     |
| Phosphonic acid   | 25          | 27.3%             | 0.98 | 72%        | 23%               | 0.82 | –   | 28%       | –                 | –    | 1   |



## Impact of ILIS on improving trueness



### Average CVs\*

w. ILIS

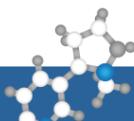
Overall

No ILIS

14

21

29



# ILIS

## €-cent per portion (exemplary)

If added to  
sample portion  
(2µg)

If added  
to 1 mL aliquot of extract  
(0.1µg)

**Chlormequat D4**

6 c

0.3 c

**Mepiquat D3**

5 c

0.3 c

**Diquat D4**

8 c

2 c

**Paraquat D6**

1 c

0.05 c

**Glyphosate 1,2-<sup>13</sup>C<sub>2</sub> <sup>15</sup>N**

5 c

0.25 c

**Ethephon D4**

17 c

0.85 c

**Fosetyl-AI D15**

8 c

0.4 c

**Maleic hydrazide D2**

12 c

0.6 c

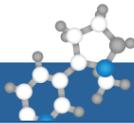
### Notes:

- If detections are rare ILIS can be added in a 2<sup>nd</sup> analysis in case of positives
- If RTs are shifting, ILIS gives additional certainty to identification.

# Compensation of Matrix Effects by IL-ISs

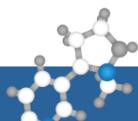
| LC-MS/MS<br>ESI (*) | Trime-<br>sium                           | Nereis-toxin | Mepiquat    | Chlormequat | Daminozide  | Cyromazin   | AVG<br>(w/o Trimesium) |
|---------------------|------------------------------------------|--------------|-------------|-------------|-------------|-------------|------------------------|
|                     | <b>Quantified directly via peak area</b> |              |             |             |             |             |                        |
| Oat                 | 40%                                      | 79%          | 31%         | 66%         | 76%         | 54%         | 61%                    |
| Wheat               | 27%                                      | 80%          | 17%         | 60%         | 44%         | 46%         | 49%                    |
| Barley              | 40%                                      | 71%          | 34%         | 73%         | 40%         | 44%         | 52%                    |
| Apple               | 50%                                      | 96%          | 62%         | 84%         | 72%         | 89%         | 80%                    |
| Orange              | 11%                                      | 52%          | 37%         | 38%         | 36%         | 18%         | 36%                    |
| Lemon               | 7%                                       | 41%          | 26%         | 30%         | 34%         | 17%         | 30%                    |
| Cherry              | 45%                                      | 75%          | 51%         | 73%         | 75%         | 64%         | 68%                    |
| Strawberry          | 47%                                      | 54%          | 68%         | 58%         | 83%         | 47%         | 62%                    |
| Grape 1             | 70%                                      | 83%          | 70%         | 79%         | 74%         | 82%         | 78%                    |
| Grape 2             | 68%                                      | 79%          | 76%         | 77%         | 73%         | 79%         | 77%                    |
| Grape 3             | 65%                                      | 79%          | 72%         | 69%         | 65%         | 54%         | 68%                    |
| Grape 4             | 62%                                      | 71%          | 68%         | 70%         | 68%         | 59%         | 67%                    |
| <b>Solvent</b>      | <b>100%</b>                              | <b>100%</b>  | <b>100%</b> | <b>100%</b> | <b>100%</b> | <b>100%</b> | <b>100%</b>            |
| <b>AVG</b>          | <b>44%</b>                               | <b>72%</b>   | <b>51%</b>  | <b>65%</b>  | <b>61%</b>  | <b>55%</b>  | <b>61%</b>             |

|                |                                                 |             |             |             |             |             |             |
|----------------|-------------------------------------------------|-------------|-------------|-------------|-------------|-------------|-------------|
|                | <b>Quantified via ILISs</b>                     |             |             |             |             |             |             |
| Oat            | <b>No ISTD available<br/>in this experiment</b> | 103%        | 94%         | 99%         | 98%         | 100%        | 99%         |
| Wheat          |                                                 | 106%        | 95%         | 98%         | 97%         | 101%        | 99%         |
| Barley         |                                                 | 105%        | 94%         | 99%         | 108%        | 103%        | 102%        |
| Apple          |                                                 | 104%        | 98%         | 100%        | 90%         | 104%        | 99%         |
| Orange         |                                                 | 108%        | 96%         | 101%        | 94%         | 107%        | 101%        |
| Lemon          |                                                 | 115%        | 97%         | 98%         | 78%         | 110%        | 100%        |
| Cherry         |                                                 | 103%        | 95%         | 103%        | 84%         | 104%        | 98%         |
| Strawberry     |                                                 | 118%        | 98%         | 95%         | 99%         | 106%        | 103%        |
| Grape 1        |                                                 | 104%        | 99%         | 101%        | 83%         | 104%        | 98%         |
| Grape 2        |                                                 | 104%        | 100%        | 102%        | 81%         | 107%        | 99%         |
| Grape 3        |                                                 | 110%        | 100%        | 100%        | 81%         | 105%        | 99%         |
| Grape 4        |                                                 | 105%        | 97%         | 98%         | 94%         | 105%        | 100%        |
| <b>Solvent</b> |                                                 | <b>100%</b> | <b>100%</b> | <b>100%</b> | <b>100%</b> | <b>100%</b> | <b>100%</b> |
| <b>AVG</b>     | <b>107%</b>                                     | <b>97%</b>  | <b>99%</b>  | <b>91%</b>  | <b>105%</b> | <b>100%</b> |             |

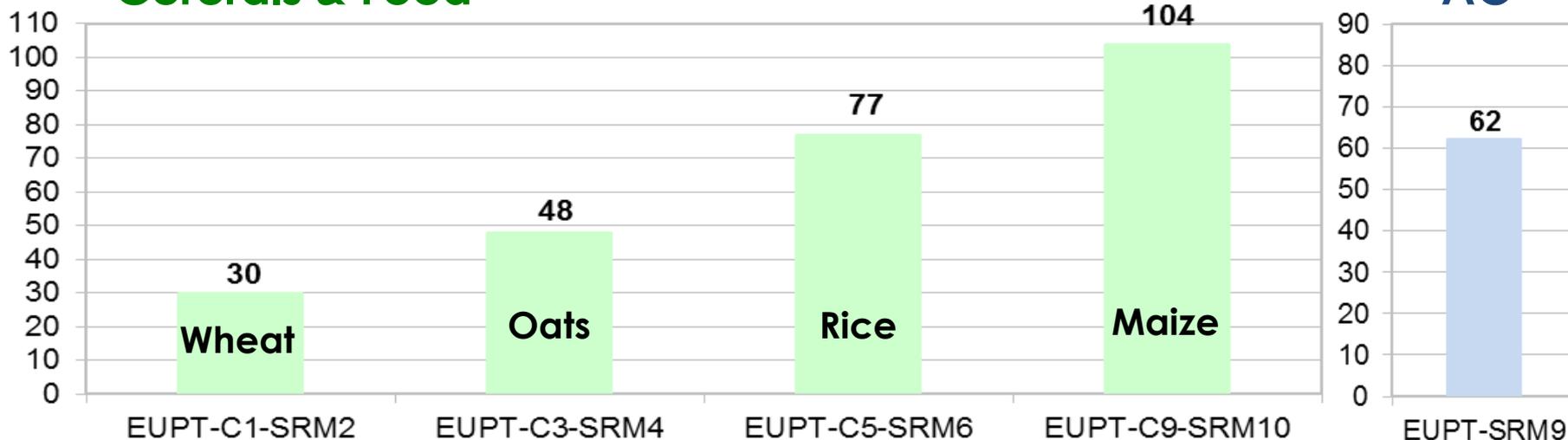


# **EUPT-SRM 1– 10**

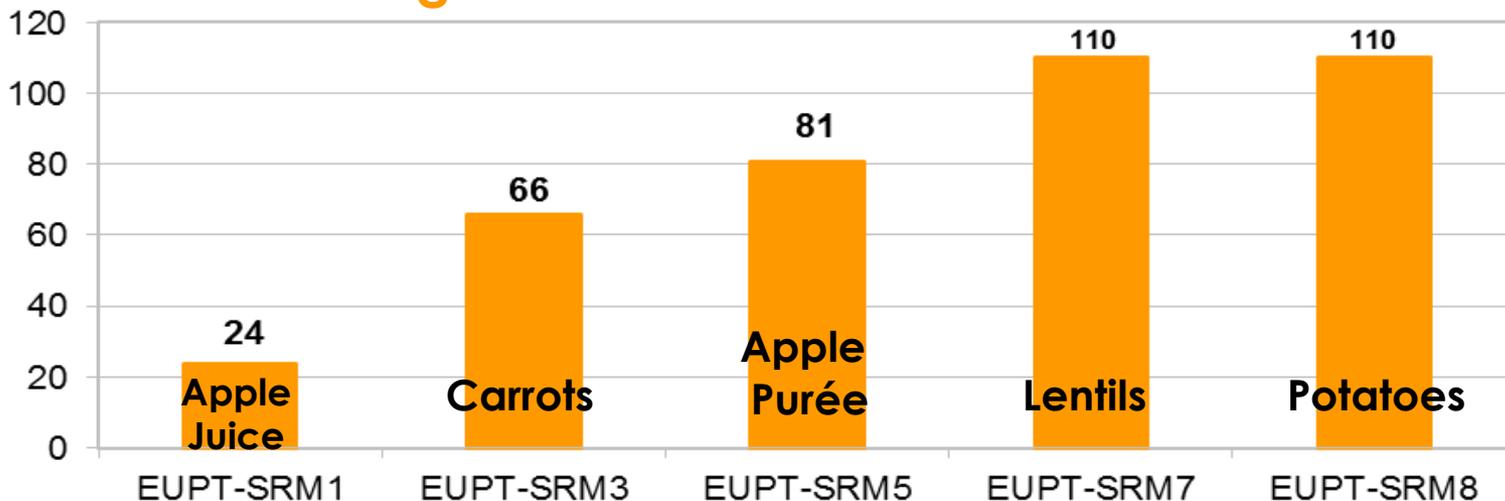
## **Overall Evaluation**

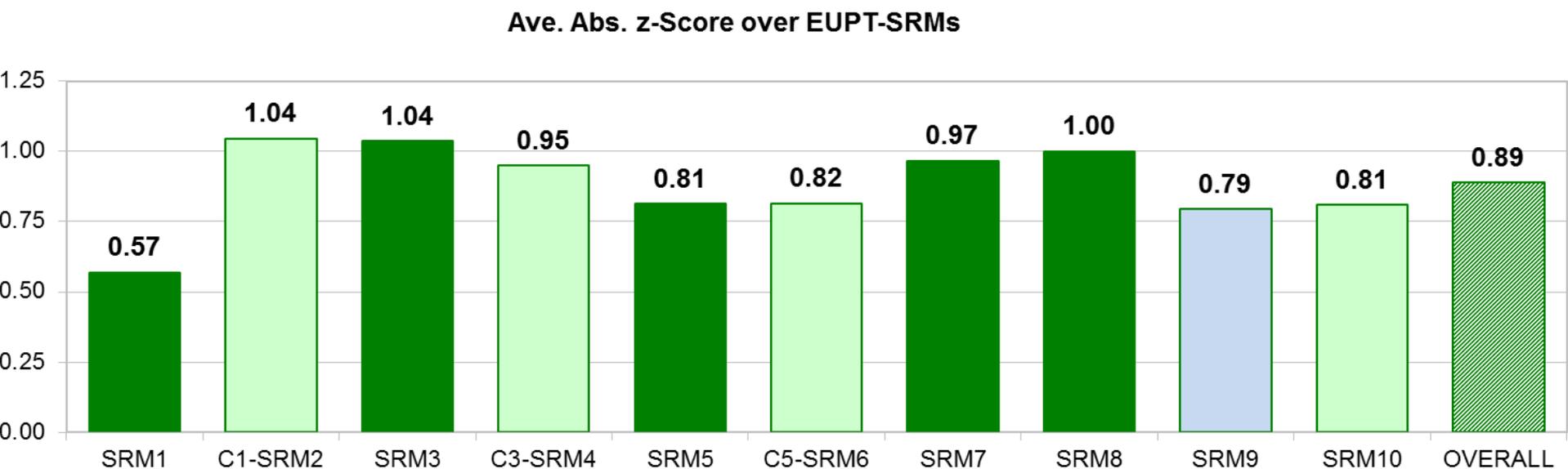
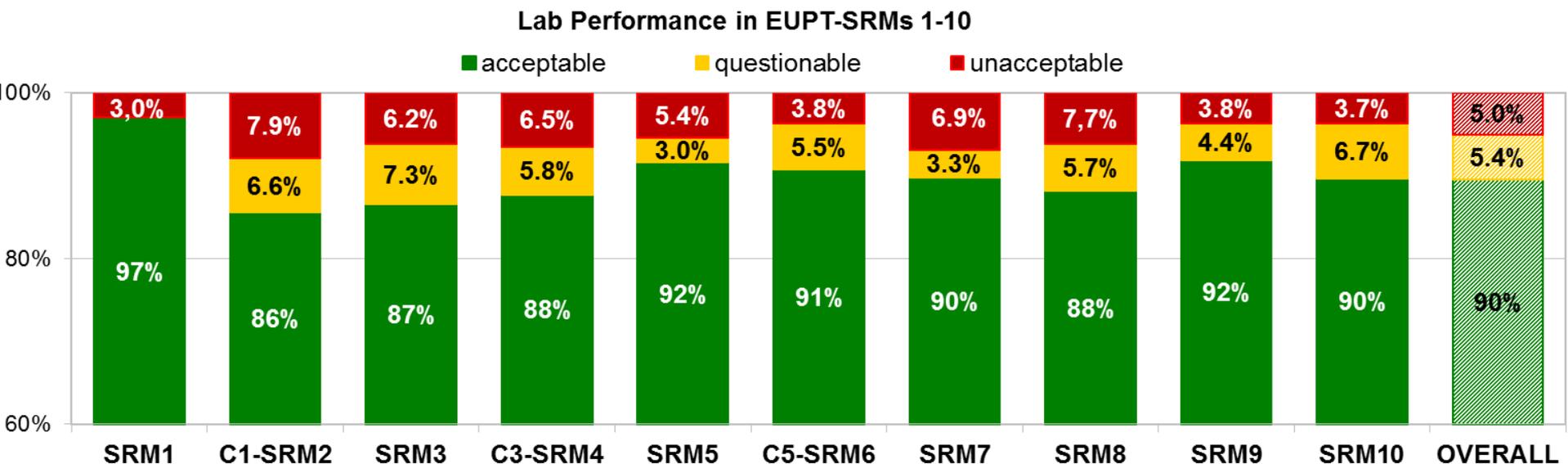


### Cereals & Feed

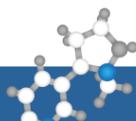


### Fruits & Vegetables

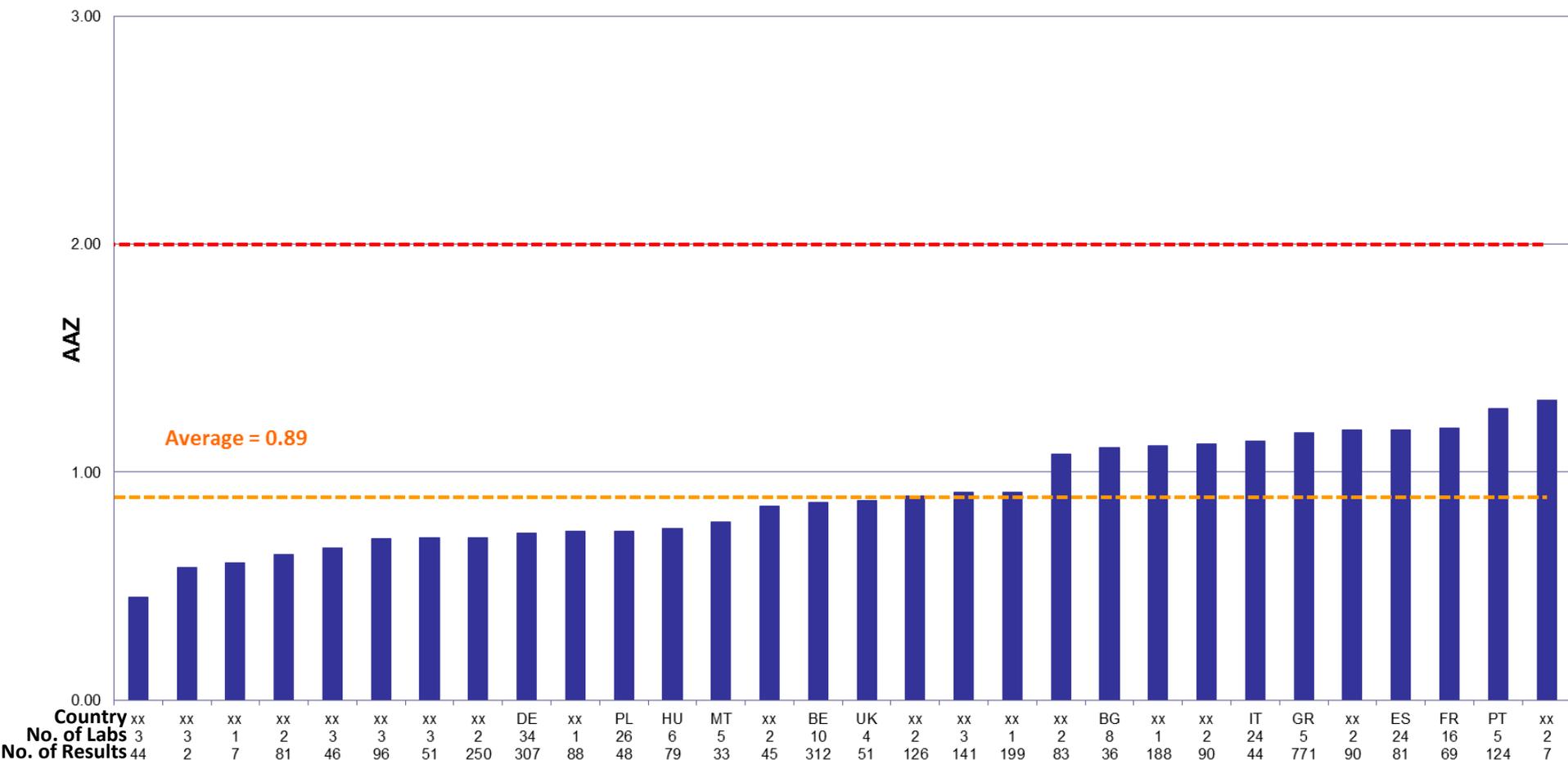




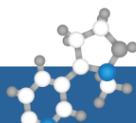
**Analytes that were evaluated for information only were excluded.**



Average of Abs. z-Scores (AAZ) in EUPT-SRMs 1-10



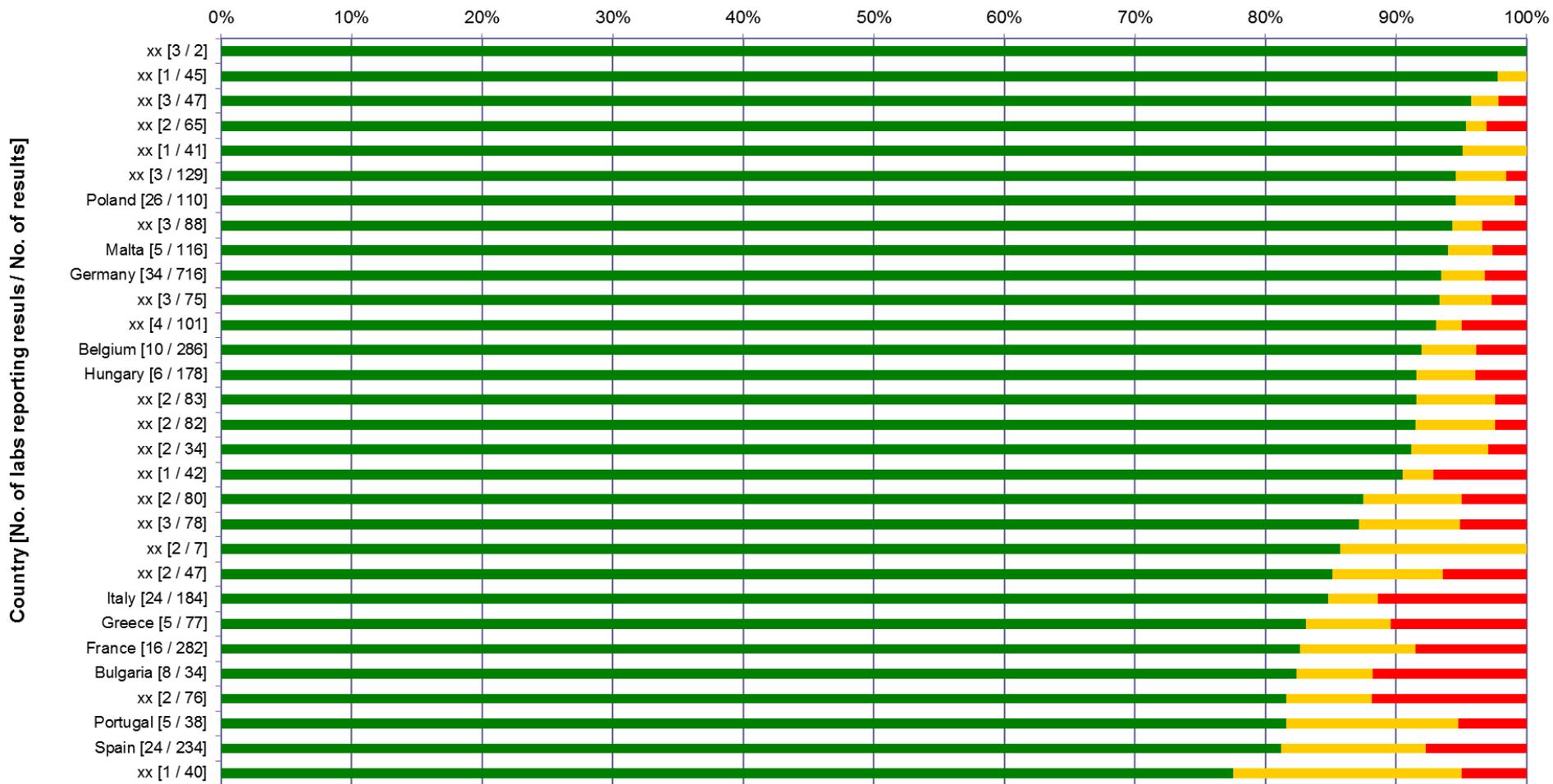
Analtes evaluated for information only were excluded from the AAZ-calculation but considered in the No. of results.  
 Countries with less than 4 labs participating in the EUPT-SRM 1-10 are hidden



# PERFORMANCE BY COUNTRY (EUPT-SRM 1-10)

Percentage of results by classification (EUPT-SRM1-10)

■ Acceptable ■ Questionable ■ Unacceptable



**Analytes evaluated for information only were excluded.**  
**Countries with less than 4 labs participating in the EUPT-SRM 1-10 are hidden.**



# Thank You for Your Attention



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