3rd Latin American Pesticide Residue Workshop

Radisson Montevideo Victoria Plaza Hotel / Montevideo / URUGUAY
8-11 de Mayo, 2011

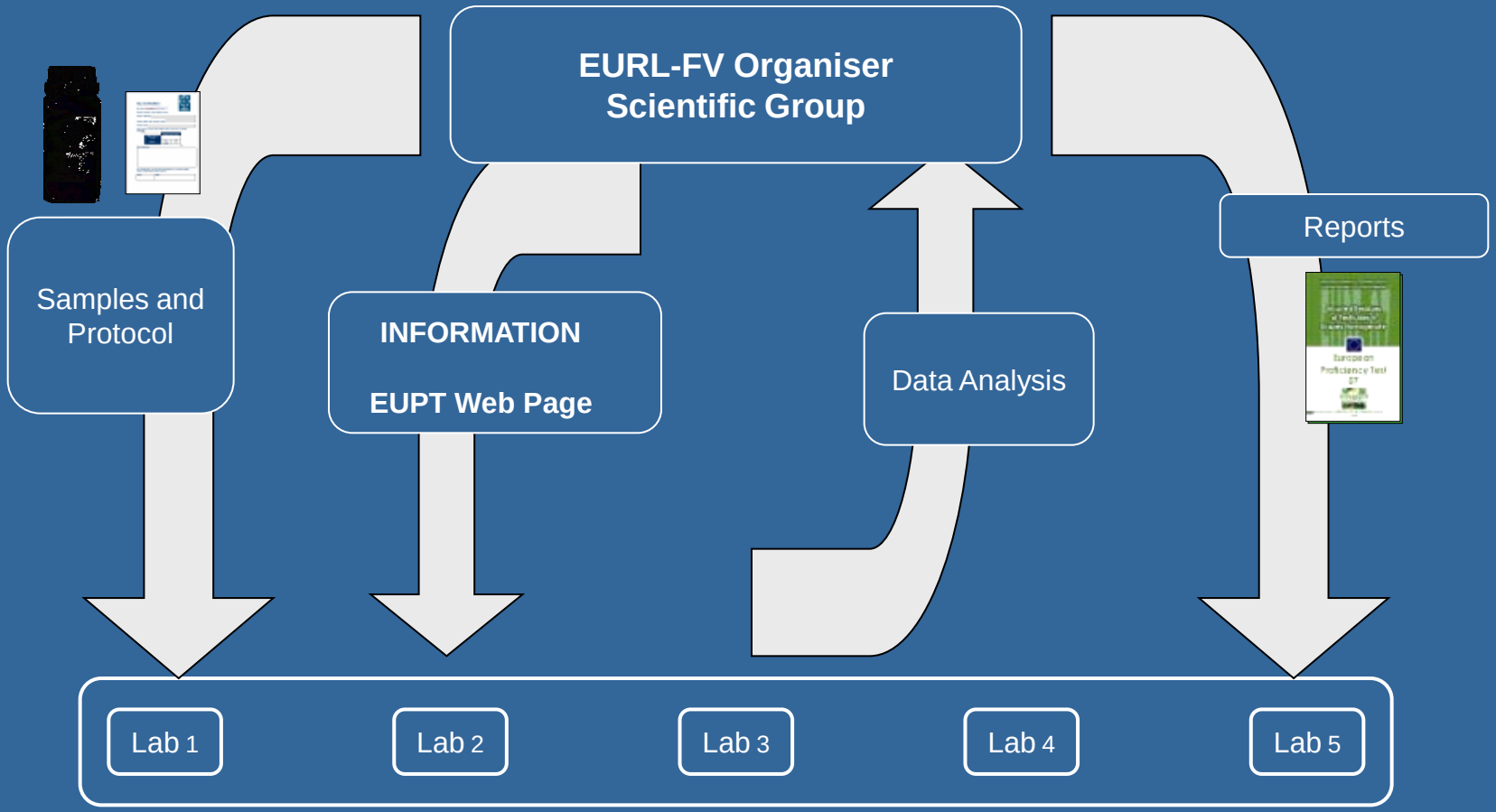
EURL
European Union Reference Laboratory
for Pesticide Residues in Fruits & Vegetables

Analytical quality control aspects achieved from EUPT-FV database

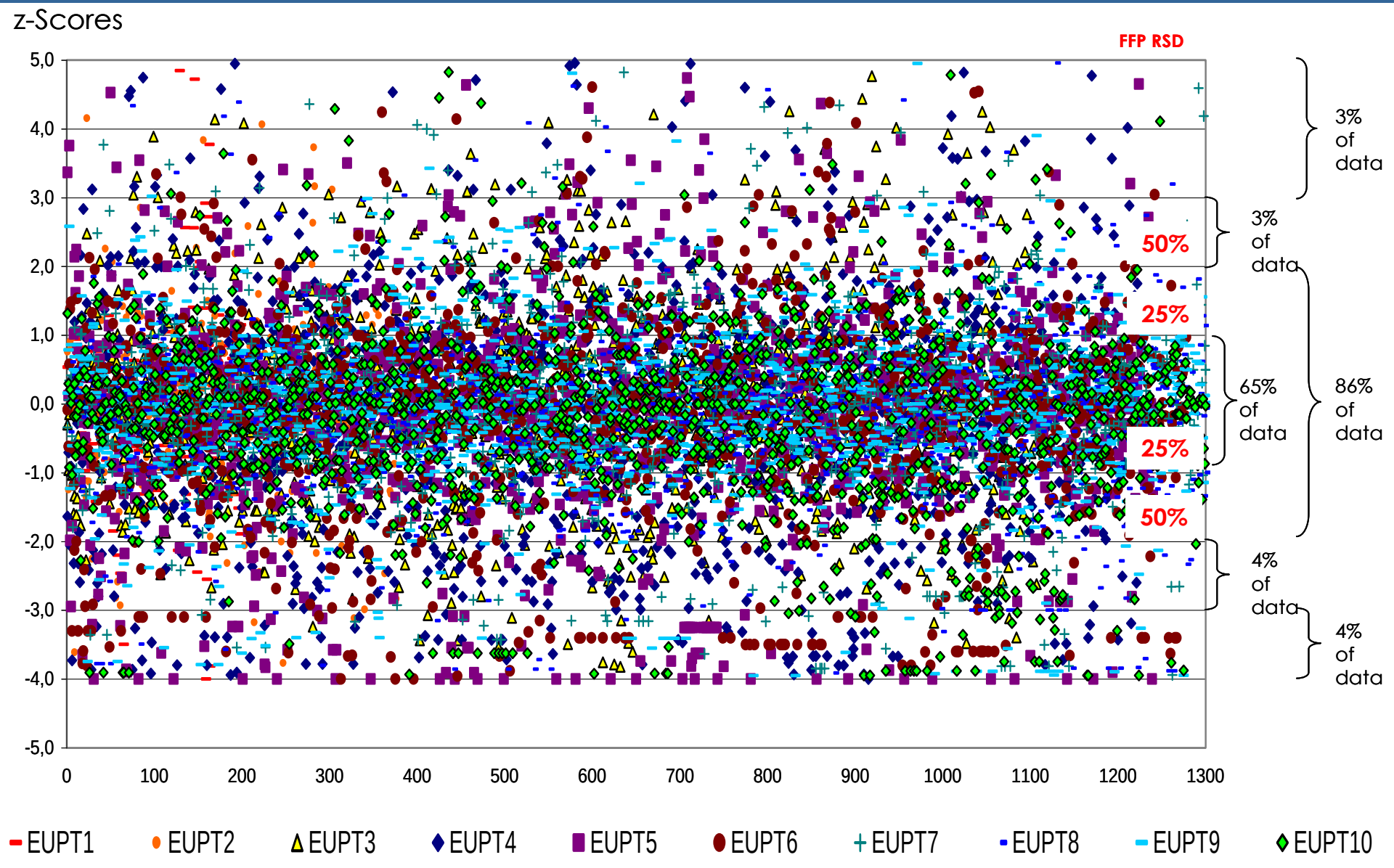
Paula Medina Pastor

EUPT-FV

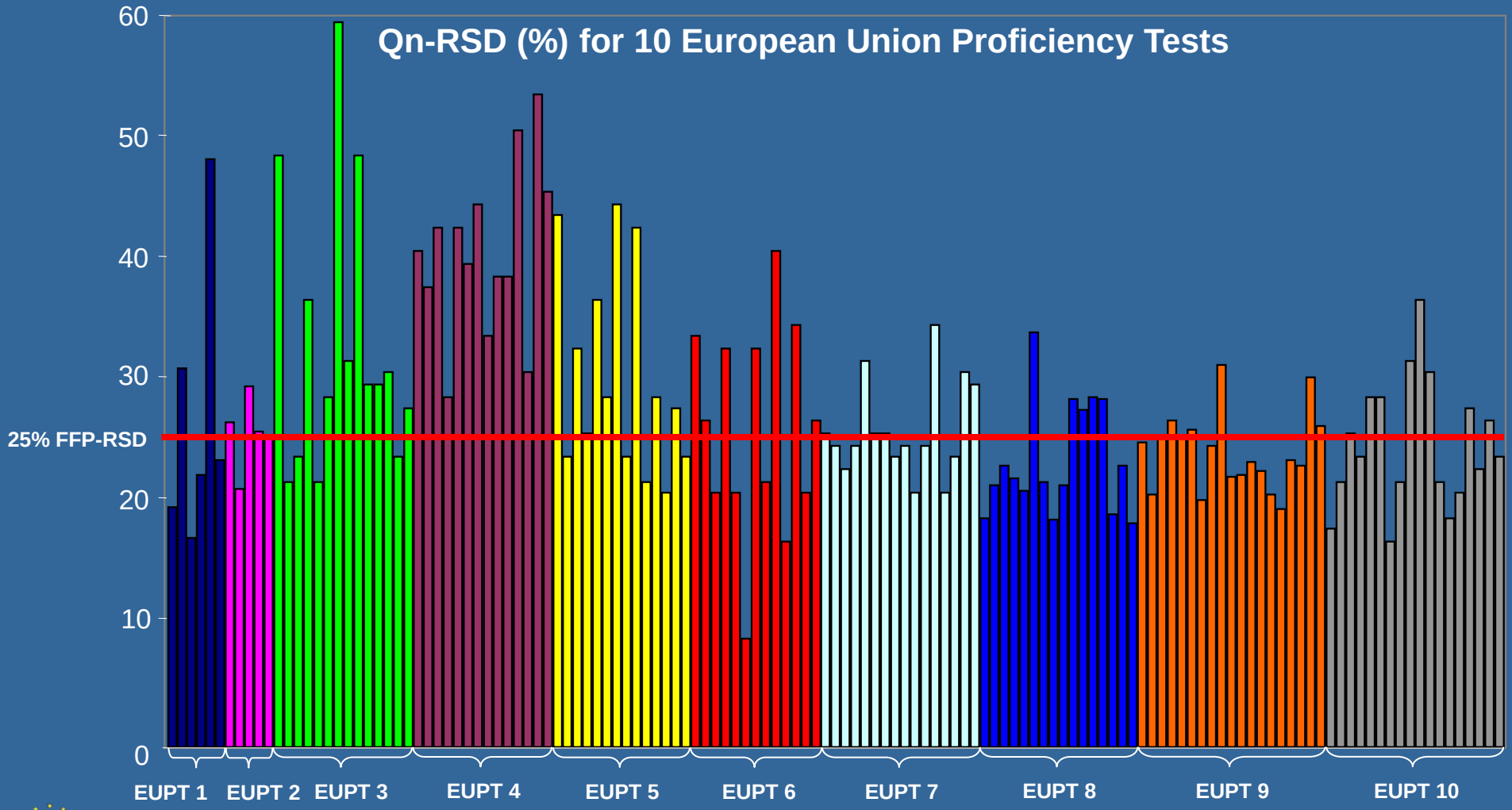
General European Union Proficiency Test Scheme



Summary of z-Score Results for 10 EUPT-FVs: 12753 points



The FFP-RSD of 25% used



$$z = (x-X) / \sigma$$

- x The result reported by the participant laboratory, or the MRRL for those laboratories not having detected the presence of the pesticide in the sample.
- X The assigned value or median value, after taking out results very far from the central population.
- σ The target standard deviation (= FFP RSD of 25%, multiplied by the assigned value)

$\|z\| \leq 2$	**Acceptable**
$2 < \|z\| \leq 3$	**Questionnable**
$3 < \|z\|$	**Unacceptable**

Classification A and B

- Category A Laboratories needed to demonstrate a 'sufficient scope' by:
  - detect at least 90% of the pesticides present in the sample.
  - report no false positives.

- The rest are in Category B

The Sum Weighted z-Score

$$|SWZ| = \frac{\sum_{i=1}^{n} |Z_i| \omega(Z_i)}{n}$$

$$\omega|Z_i| = \begin{cases} 1 & \text{if} \quad |Z| \leq 2 \\ 3 & \text{if} \quad 2 < |Z| \leq 3 \\ 5 & \text{if} \quad |Z| > 3 \end{cases}$$

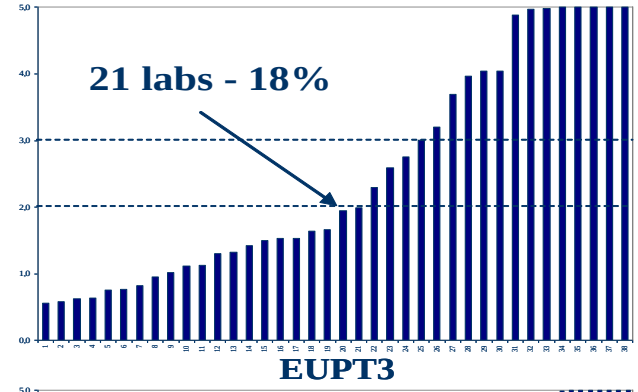
Classification:

|SWZ| ≤ 2 Good
2 < |SWZ| ≤ 3 Satisfactory
|SWZ| > 3 Unsatisfactory

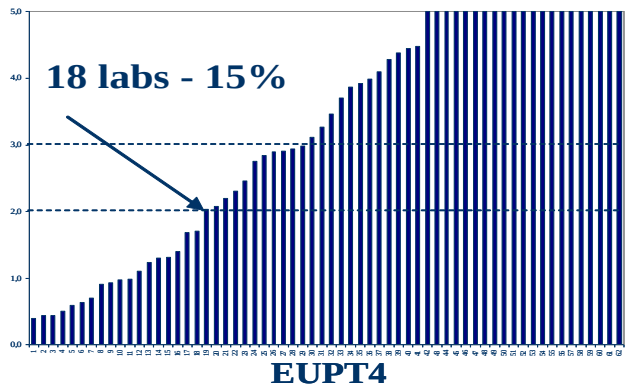
Advantages:

- **classification are as z-score**
- **differences are made upon z-score results**
- **making them comparable through the years**

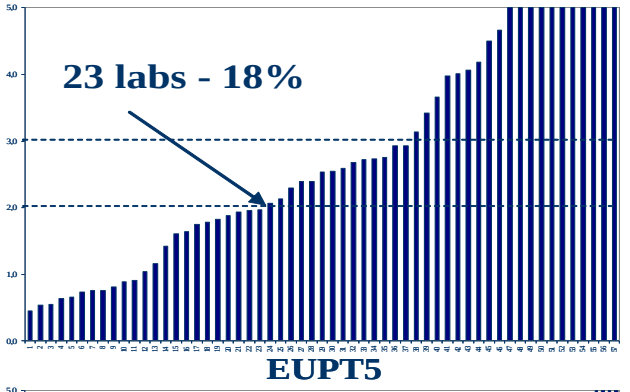
The Combined z-Scores



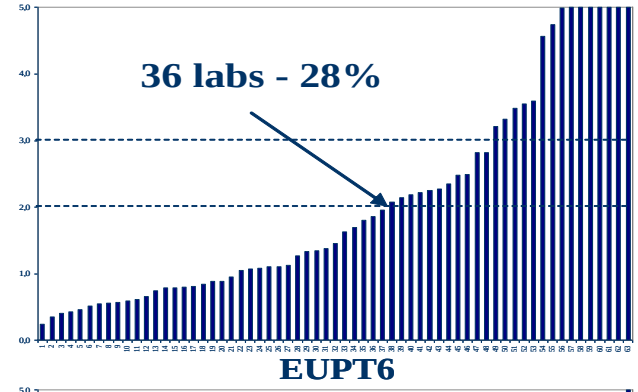
EUPT3



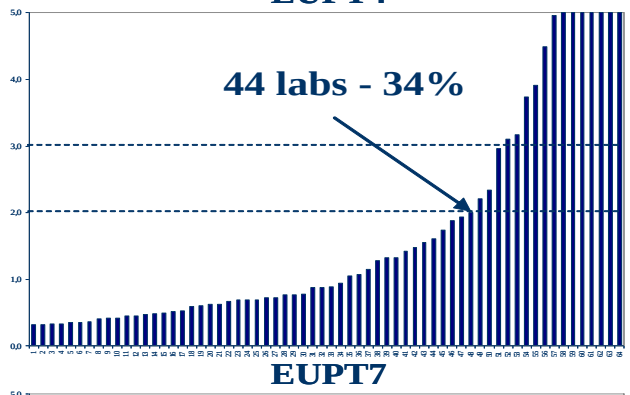
EUPT4



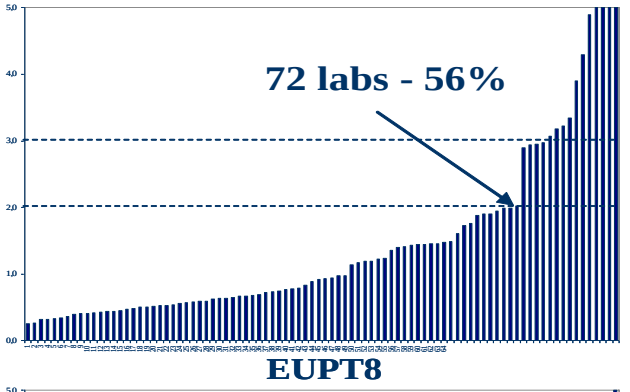
EUPT5



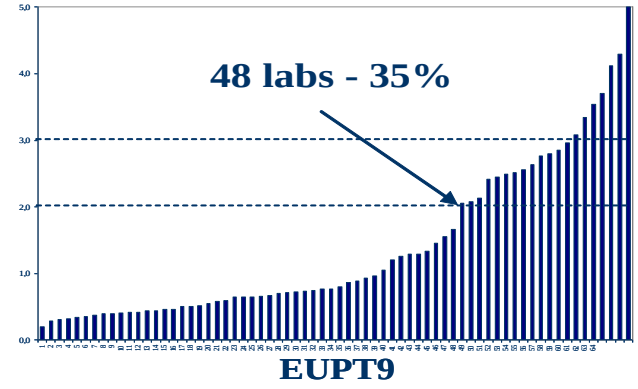
EUPT6



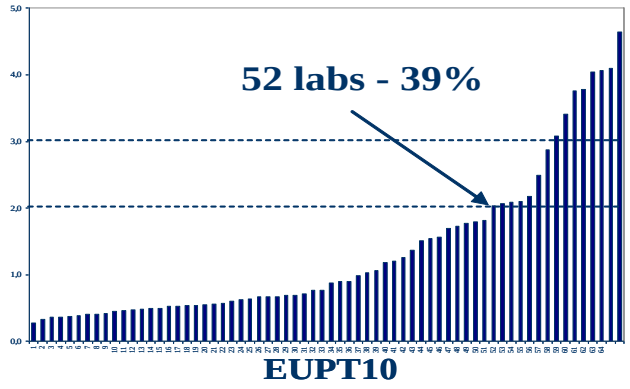
EUPT7



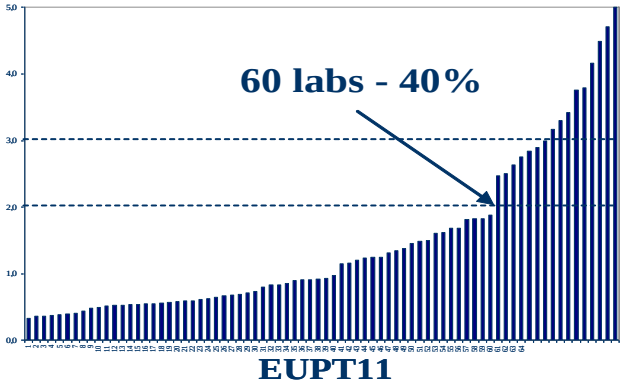
EUPT8



EUPT9



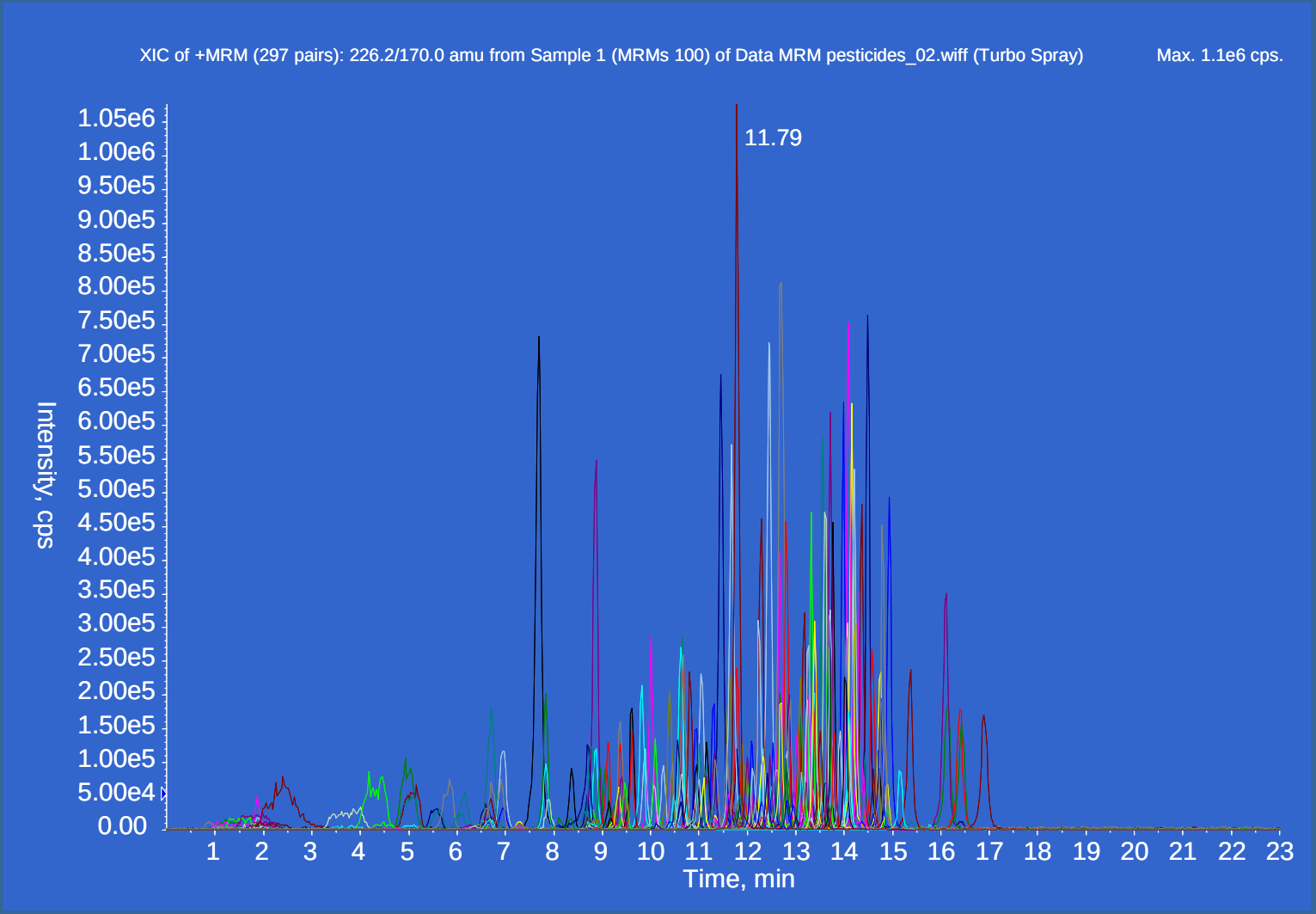
EUPT10



EUPT11

Analytical quality control aspects achieved

Multiresidue Methods



Scope

EUPT-FV Scope – EU Coordinated Plan

144 pesticides

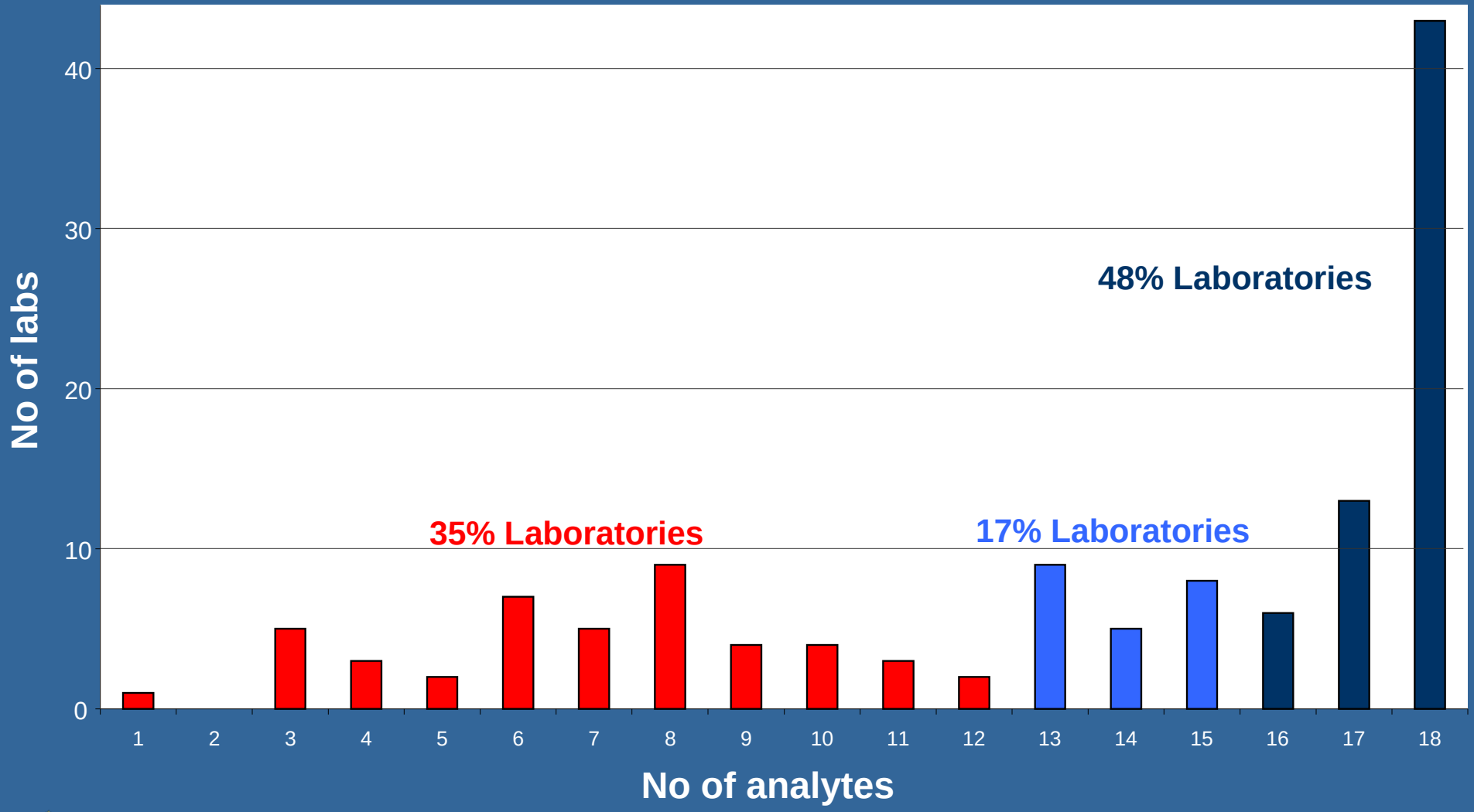
Fixed MRRL = 0.01mg/kg

- Acephate
- Acetamiprid
- Acrinathrin
- Aldicarb (sum)
- Amitraz
- DMPF
- DMF
- Azinphos-methyl
- Azoxystrobin
- Benfuracarb
- Bifenthrin
- Bitertanol
- Boscalid
- Bromopropylate
- Bromuconazole
- Bupirimate
- Buprofezin
- Cadusafos
- Captan
- Carbaryl
- Carbendazim (sum)
- Carbofuran (sum)
- Carbosulfan
- Chlorfenapyr
- Chlorfenvinphos
- Chlorobenzilate
- Chlorothalonil
- Chlorpropham
- Chlorpyrifos
- Chlorpyrifos-methyl
- Clofentezine
- Cyfluthrin
- Cypermethrin (sum)
- Cyproconazole
- Cyprodinil
- Deltamethrin
- Diazinon
- Dichlofluanid
- Dichlorvos
- Dicloran
- Dicofol
- Difenoconazole
- Dimethoate (sum)
- Dimethomorph
- Diphenylamine
- Endosulfan (sum)
- EPN
- Epoxiconazole
- Ethion
- Etofenprox
- Ethoprophos
- Fenamiphos (sum)
- Fenarimol
- Fenazaquin
- Fenbuconazole
- Fenhexamid
- Fenitrothion
- Fenoxycarb
- Fenpropathrin
- Fenpropimorph
- Fenthion (sum)
- Fipronil
- Fludioxonil
- Flufenoxuron
- Fluquinconazole
- Flusilazole
- Flutriafol
- Folpet
- Fosthiazate
- Hexaconazole
- Hexythiazox
- Imazalil
- Imidacloprid
- Indoxacarb
- Iprodione
- Iprovalicarb
- Isofenphos-methyl
- Kresoxim-methyl
- Lambda-Cyhalothrin
- Linuron
- Lufenuron
- Malathion (sum)
- Mepanipyrim
- Metalaxyl and metalaxyl-M
- Metaflumizone
- Metconazole
- Methamidophos
- Methidathion
- Methiocarb (sum)
- Methomyl (sum)
- Methoxyfenozide
- Monocrotophos
- Myclobutanil
- Orthophenylphenol
- Oxadixyl
- Oxamyl
- Oxydemeton-methyl (sum)
- Paclobutrazole
- Parathion-ethyl
- Parathion-methyl (sum)
- Pencycuron
- Penconazole
- Pendimethalin
- Phenthoate
- Phosalone
- Phosmet (sum)
- Phoxim
- Pyraclostrobin
- Pirimicarb (sum)
- Pirimiphos-methyl
- Prochloraz
- Procymidone
- Profenofos
- Propargite
- Propiconazole
- Propyzamide
- Prothioconazole
- Prothiofos
- Pyridaben
- Pyrimethanil
- Pyriproxyfen
- Quinoxyfen
- Spinosad (sum)
- Spiroxamine
- Tau-Fluvalinate
- Tebuconazole
- Tebufenozide
- Tebufenpyrad
- Teflubenzuron
- Tefluthrin
- Tetraconazole
- Tetradifon
- Thiabendazole
- Thiamethoxam (sum)
- Thiacloprid
- Thiophanate-methyl
- Tolclofos-methyl
- Tolylfluanid
- Triadimefon and Triadimenol (sum)
- Triazophos
- Trichlorfon
- Trifloxystrobin
- Triflumuron
- Trifluralin
- Triticonazole
- Vinclozolin
- Zoxamide

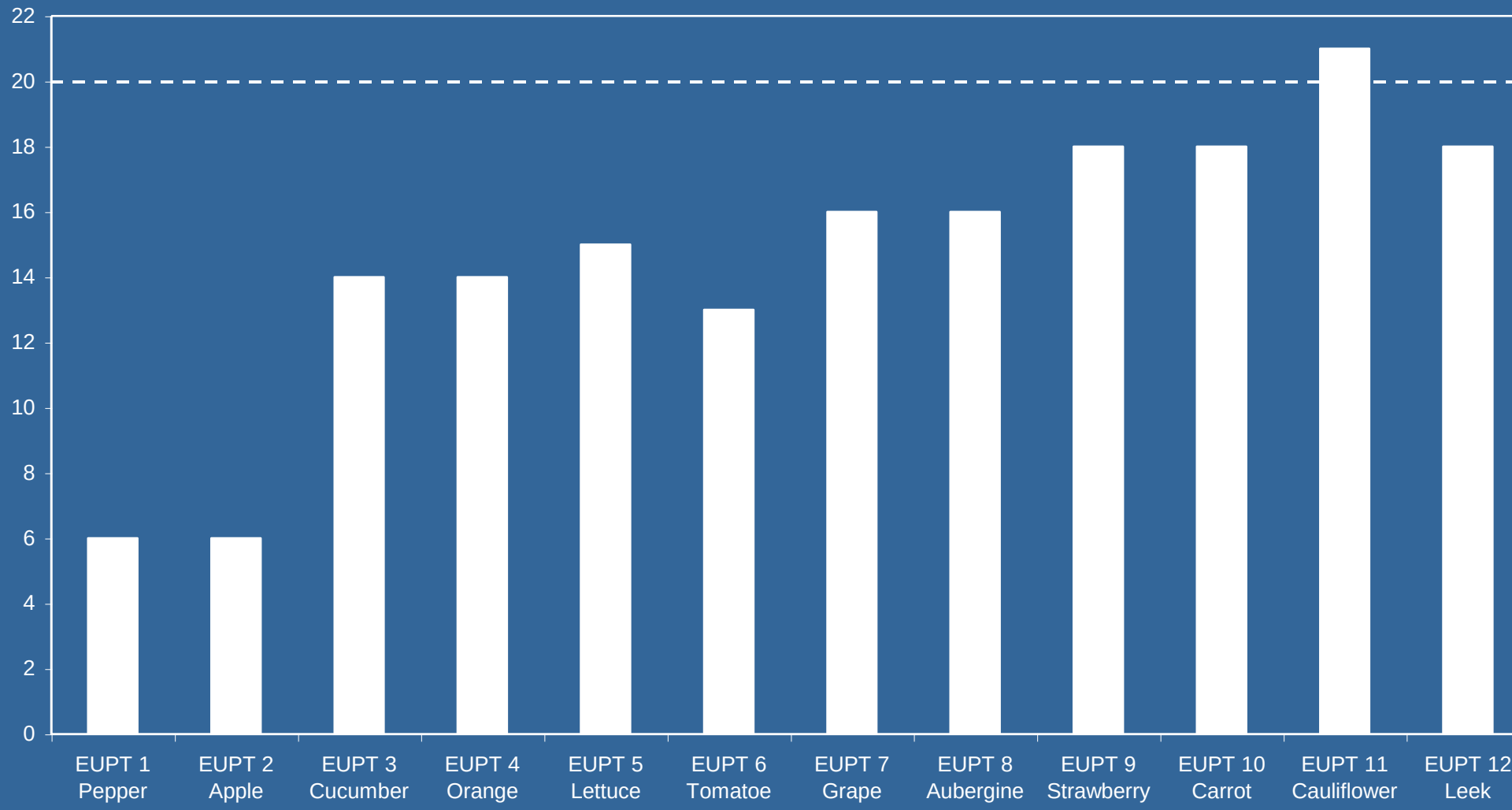
- Pesticide used in FV12 -	
Aldicarb sulfone	Fenpropathrin
Amitraz	Imidacloprid
Azinphos-methyl	Kresoxim-methyl
Cadusafos	Methamidophos
Carbendazim	Omethoate
Chlorothalonil	Oxamyl
Chlorpyrifos-ethyl	Thiacloprid
EPN*	Prothiofos*
Ethion	Triflumuron

**** Not in the monitoring plan but present in Regulation 669/2009 due to the high no. of positive findings as sanitary alarms in imported food to the EU.***

EUPT-FV10


No of labs
0
10
20
30
40
48% Laboratories
35% Laboratories
17% Laboratories
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
No of analytes

No. of Pesticides in the Sample by EUPT-FV



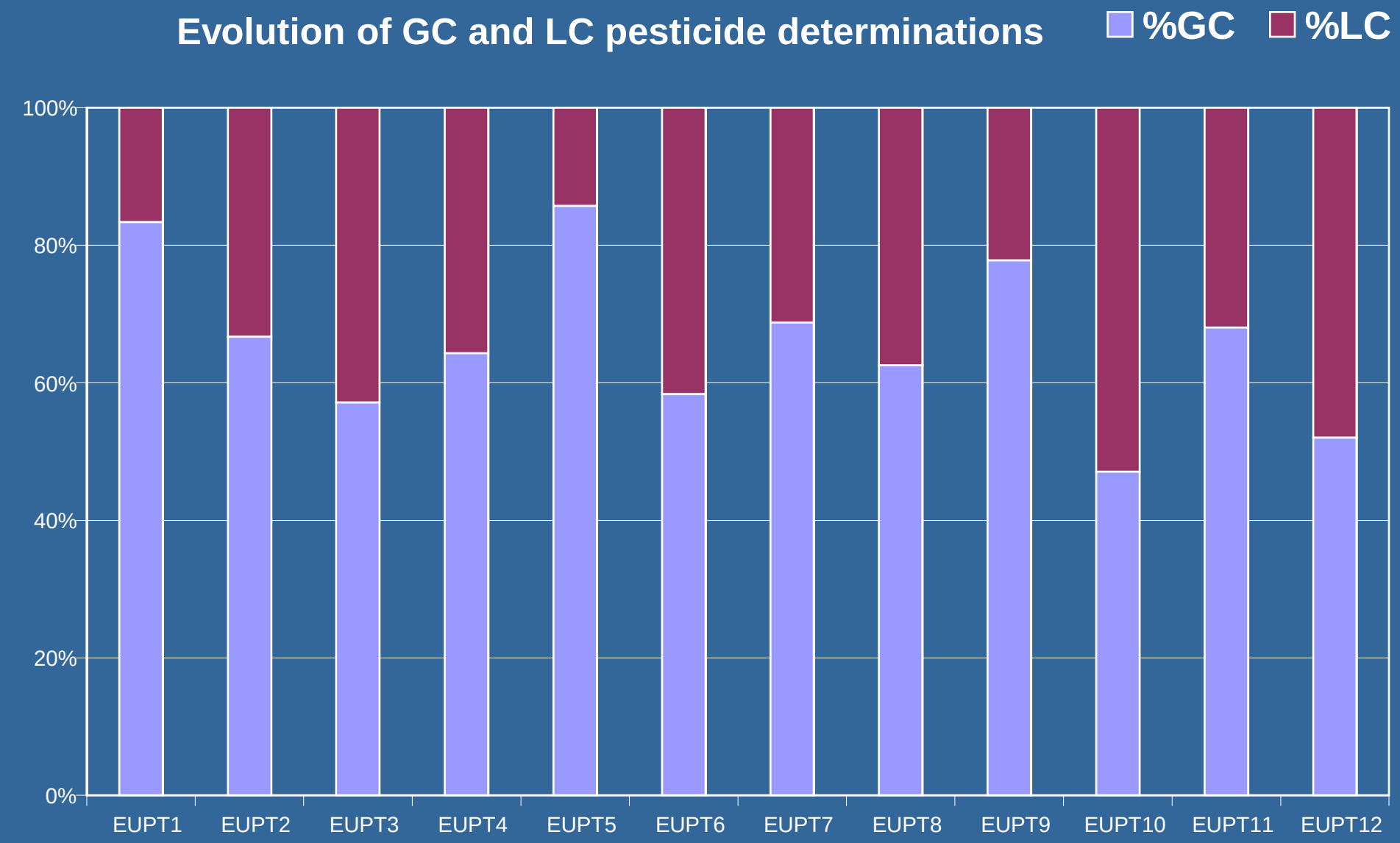
The Analytical Quality of Results

Paula Medina Pastor
10th May 2011

EUPT No.	Matrices	No. of Participating Labs.	No. of possible pesticides	No. of pesticides present in the sample	Chromatographic Techniques used (%)	
					GC	LC
1	Pepper	88	33	6	100*	0
2	Apple	85	41	6	77*	23*
3	Cucumber	116	48	14	89*	13*
4	Orange	117	57	14	96*	4*
5	Lettuce	127	57	15	96*	4*
6	Tomato	130	57	13	87	13
7	Grape	128	65	16	76	24
8	Aubergine	129	68	16	79	21
9	Strawberry	137	82	19	80	20
10	Carrot	132	113	18	66	34
11	Cauliflower	151	128	21	68	32
12	Leek	153	144	18	52	48

*More than 90% of the detectors used were ‘classical detectors’: ECD, NPD, UV…

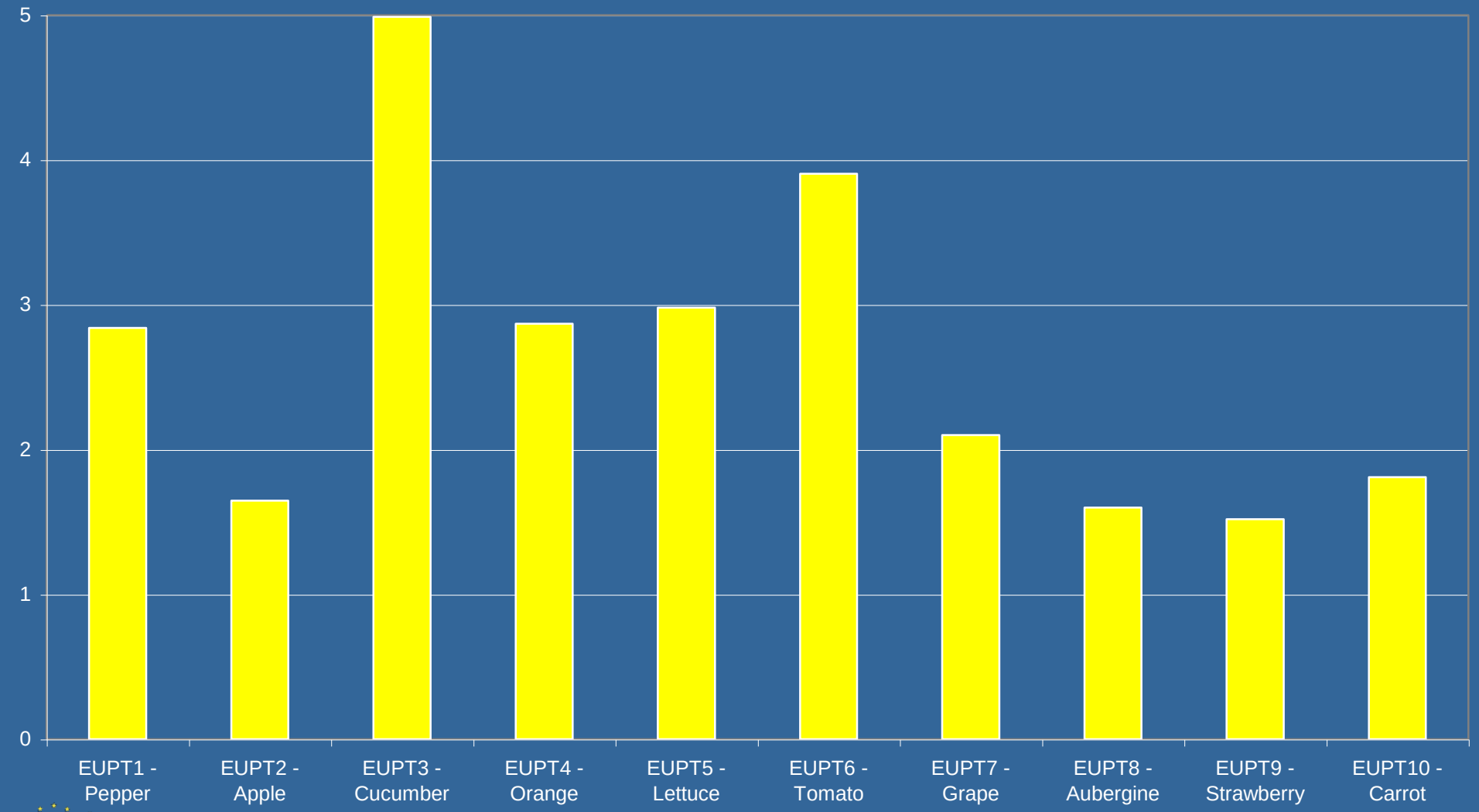
Evolution of GC and LC pesticide determinations



False Positive Results based on determination techniques

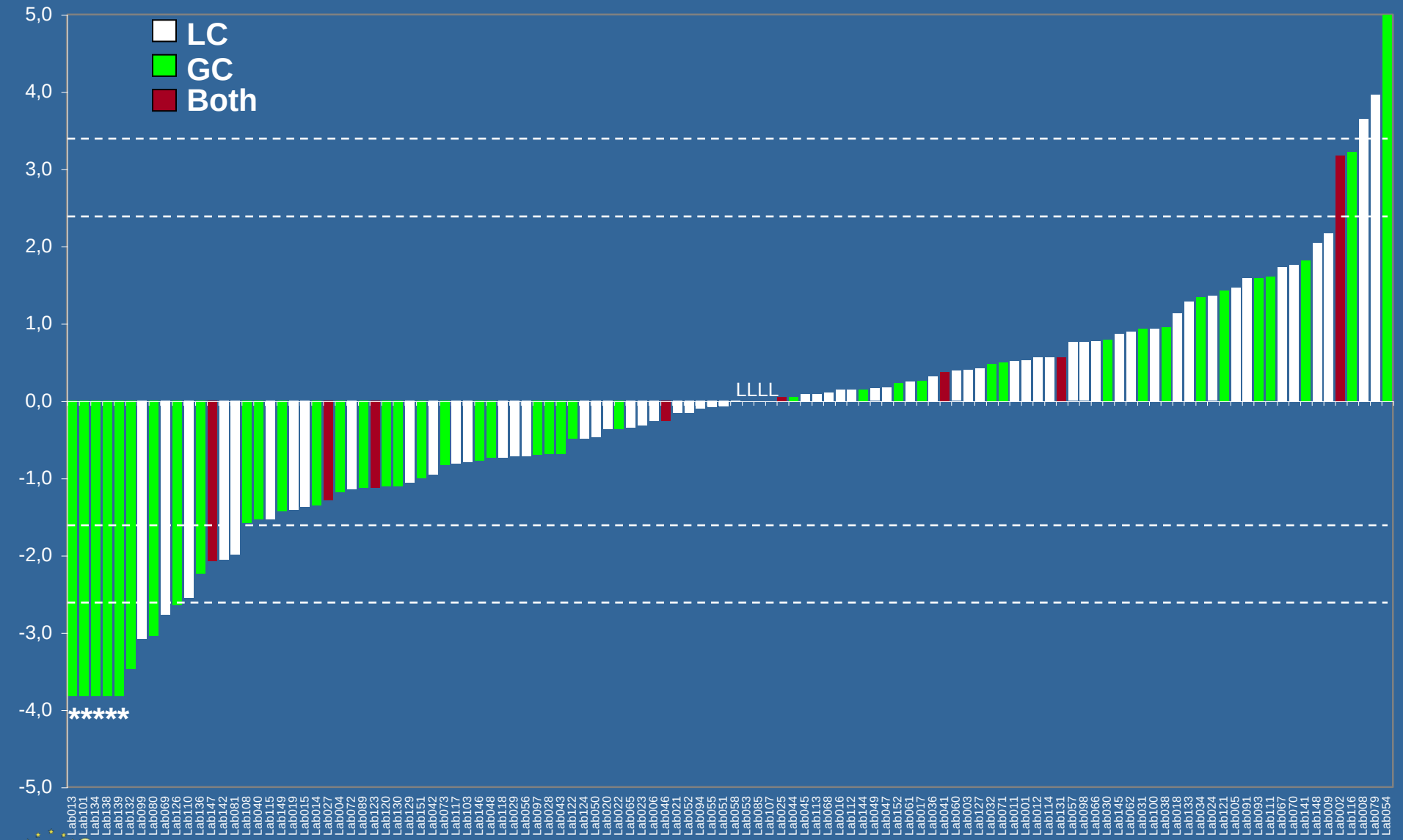
EUPT-FV	No. of False Positives	No. of False Positives by GC	No. of False Positives by LC
EUPT 1 Pepper	6	6	0
EUPT 2 Apple	6	6	0
EUPT 3 Cucumber	23	23	0
EUPT 4 Orange	15	15	0
EUPT 5 Lettuce	17	17	0
EUPT 6 Tomatoe	7	6	1
EUPT 7 Grape	6	6	0
EUPT 8 Aubergine	3	3	0
EUPT 9 Strawberry	11	9	2
EUPT 10 Carrot	8	6	2
EUPT 11 Cauliflower	11	6	5
EUPT 12 Leek	10	5	5

False Negative Results versus no. of determinations

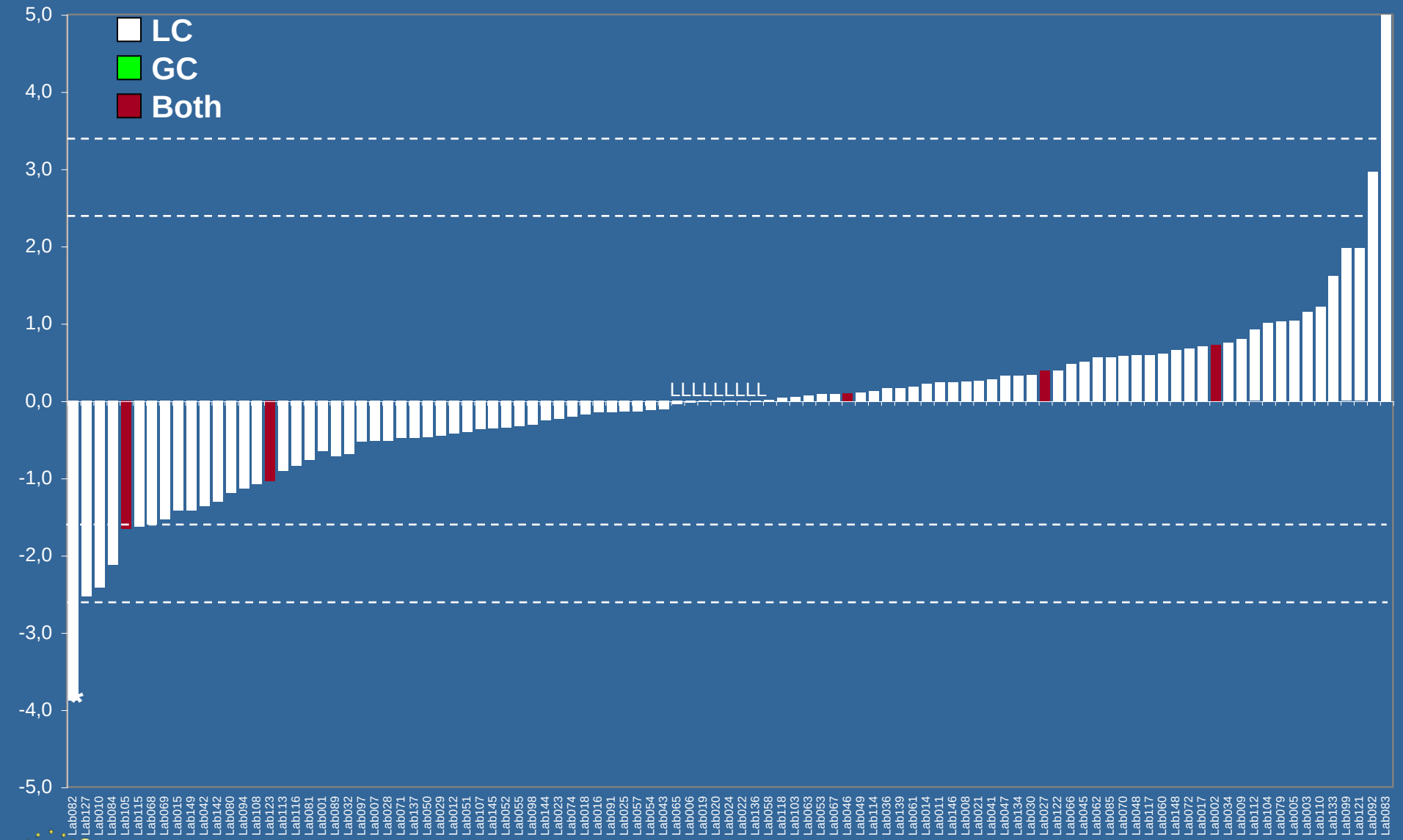


Pesticides	MRRL (mg/kg)	Median (mg/kg)	FFP RSD (%)	Qn RSD (%)
Acetamiprid	0.01	0.419	25	18
Boscalid	0.01	0.238	25	22
Chlorpyrifos-Methyl	**0.01**	**0.078**	**25**	**26**
Diazinon	0.01	0.603	25	24
Endosulfan	0.01	0.107	25	29
Hexythiazox	0.01	0.509	25	29
Isofenphos-Methyl	0.01	0.499	25	17
Kresoxim-Methyl	**0.01**	**0.050**	**25**	**22**
Malathion	0.01	0.771	25	32
Metamidophos	0.01	0.342	25	37
Methiocarb	0.01	0.157	25	31
Methomyl	0.01	0.739	25	22
Oxamyl	0.01	0.322	25	19
Pendimethalin	**0.01**	**0.074**	**25**	**21**
Phosmet	0.01	0.236	25	28
Quinoxyfen	0.01	0.298	25	23
Triadimenol	0.01	0.331	25	27
Vinclozolin	0.01	1.04	25	24

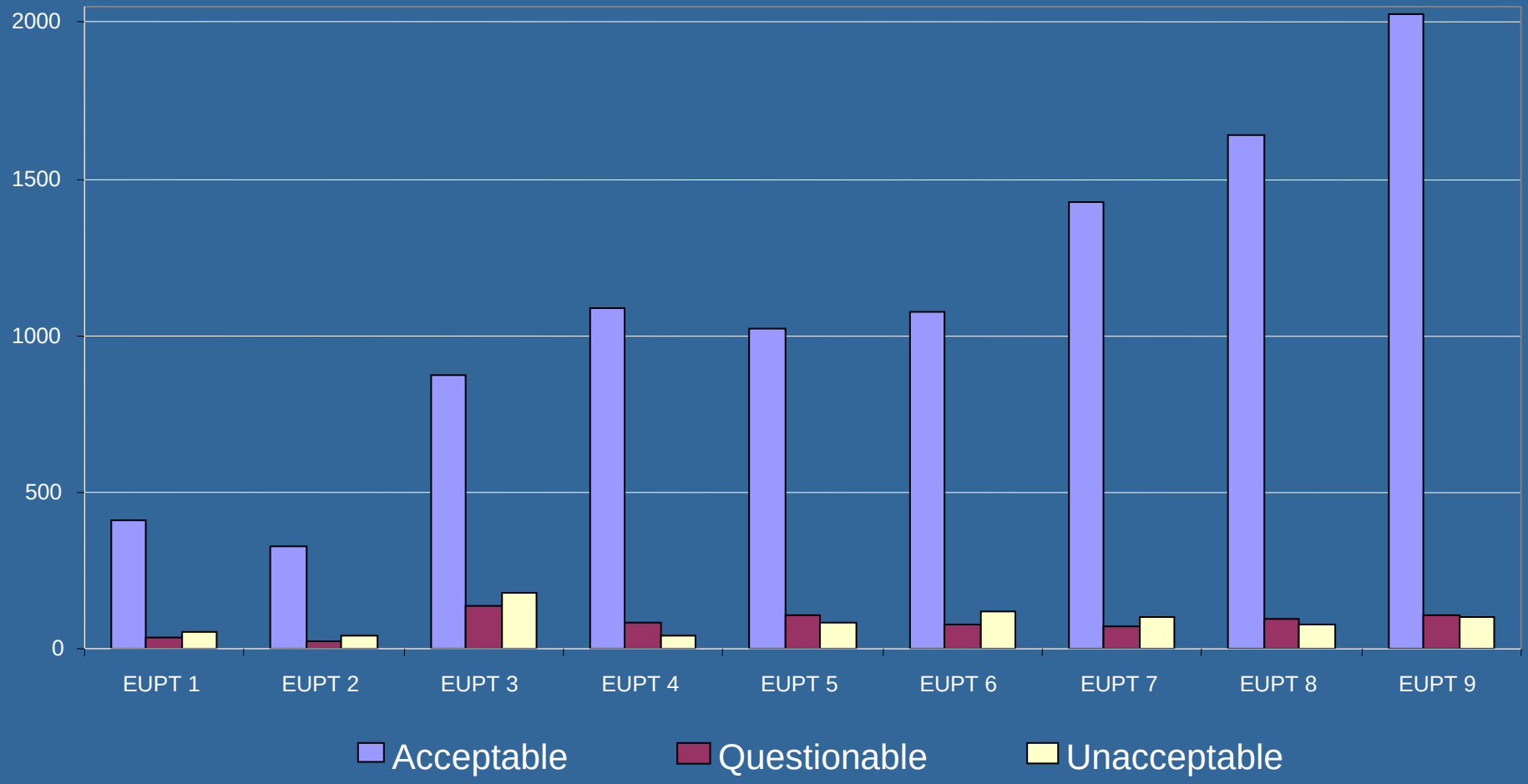
Methamidophos



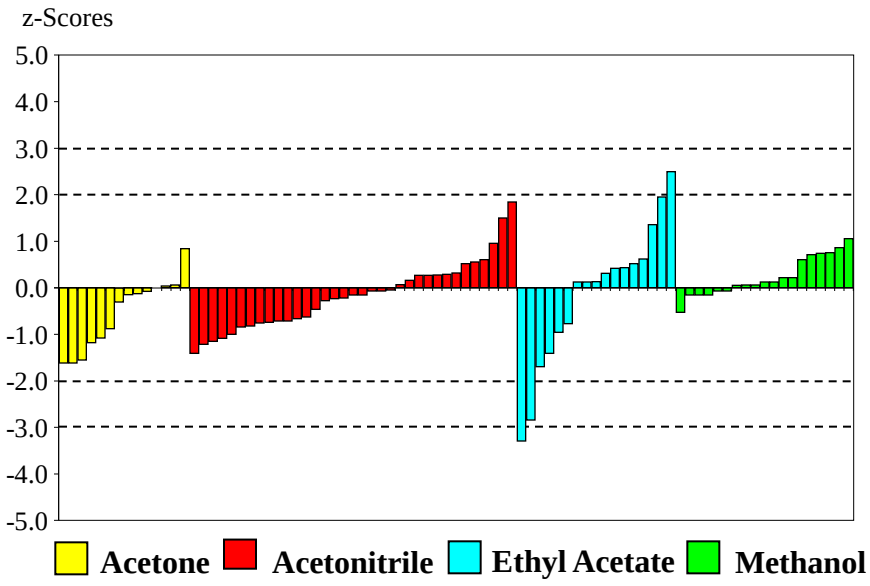
Oxamyl

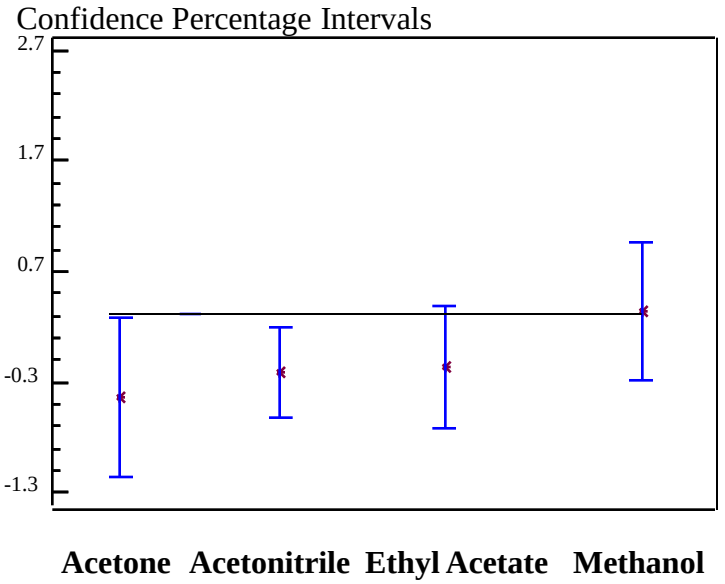

LC
GC
Both
5,0
4,0
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
LLLLLLLLL
Lab082 Lab127 Lab010 Lab084 Lab105 Lab115 Lab068 Lab069 Lab015 Lab149 Lab042 Lab142 Lab080 Lab094 Lab108 Lab123 Lab113 Lab116 Lab081 Lab001 Lab089 Lab032 Lab097 Lab007 Lab028 Lab071 Lab137 Lab050 Lab029 Lab012 Lab051 Lab107 Lab145 Lab052 Lab055 Lab098 Lab144 Lab023 Lab074 Lab018 Lab016 Lab091 Lab025 Lab057 Lab054 Lab043 Lab065 Lab006 Lab019 Lab020 Lab024 Lab022 Lab136 Lab058 Lab118 Lab103 Lab063 Lab053 Lab067 Lab046 Lab049 Lab114 Lab036 Lab139 Lab061 Lab014 Lab011 Lab146 Lab008 Lab021 Lab041 Lab047 Lab134 Lab030 Lab027 Lab122 Lab066 Lab045 Lab062 Lab085 Lab070 Lab048 Lab117 Lab060 Lab148 Lab072 Lab017 Lab002 Lab034 Lab009 Lab112 Lab104 Lab079 Lab005 Lab003 Lab110 Lab133 Lab099 Lab121 Lab092 Lab083

Global Results for the EUPTs

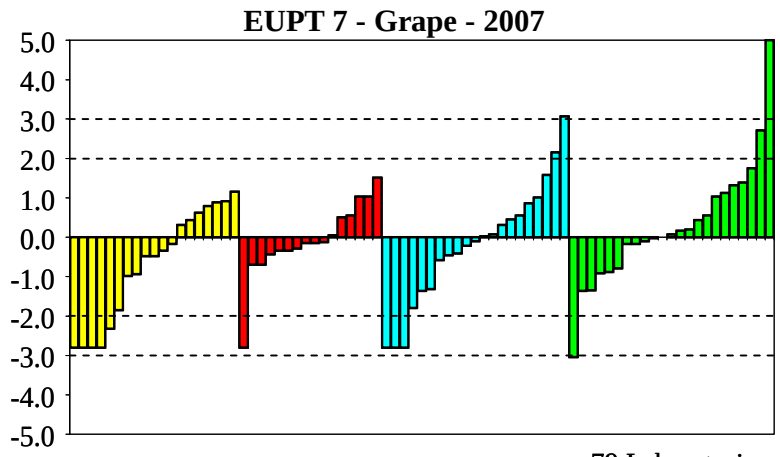


Methomyl - EUPT10 - Carrots

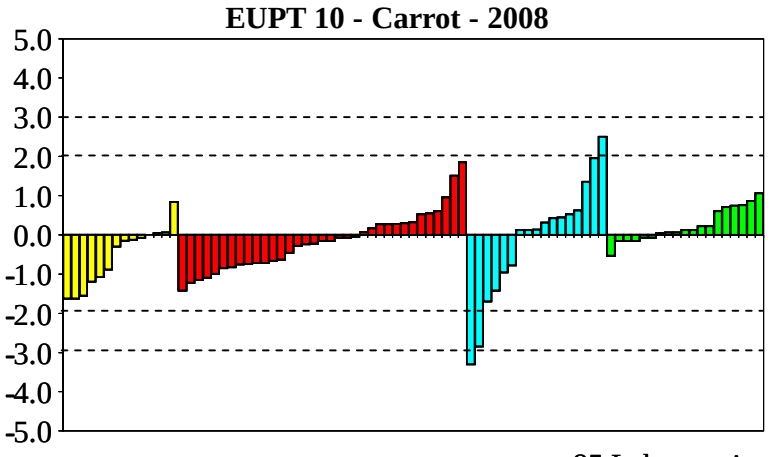




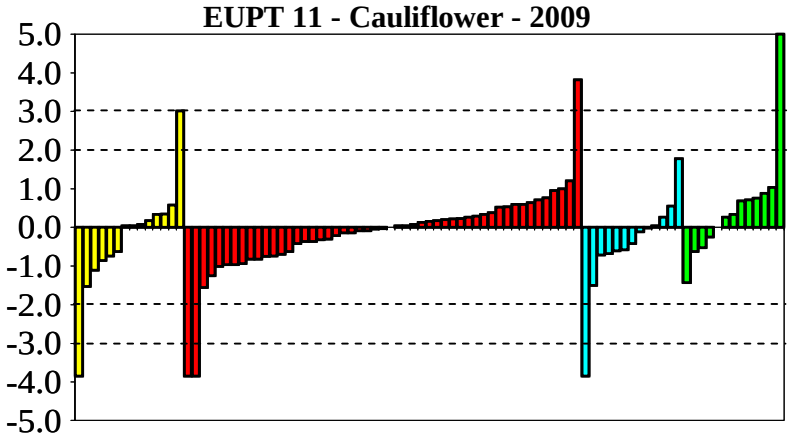
Methomyl



79 Laboratories



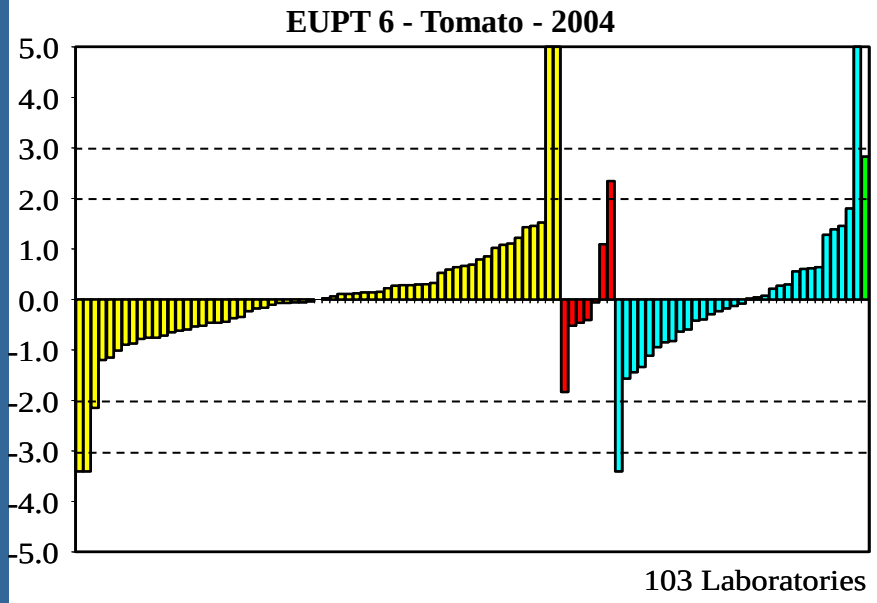
85 Laboratories

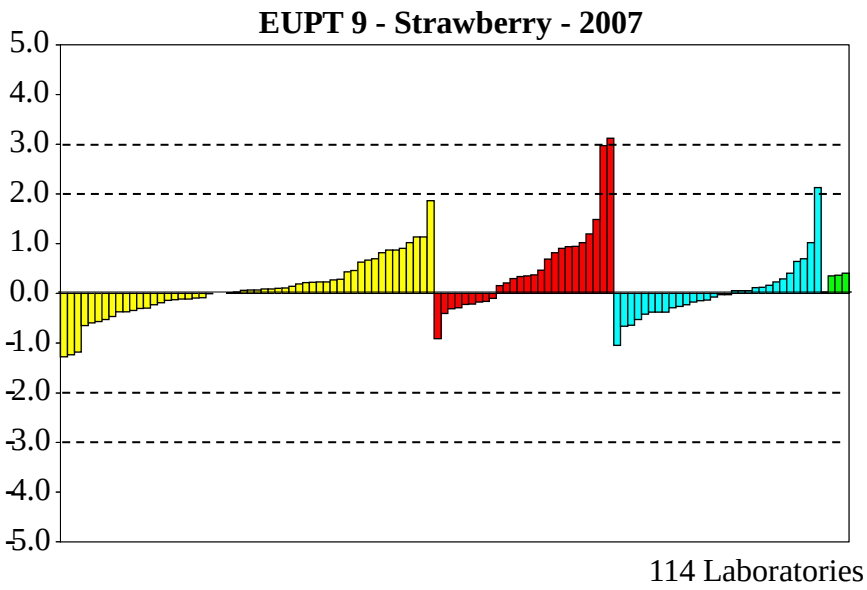


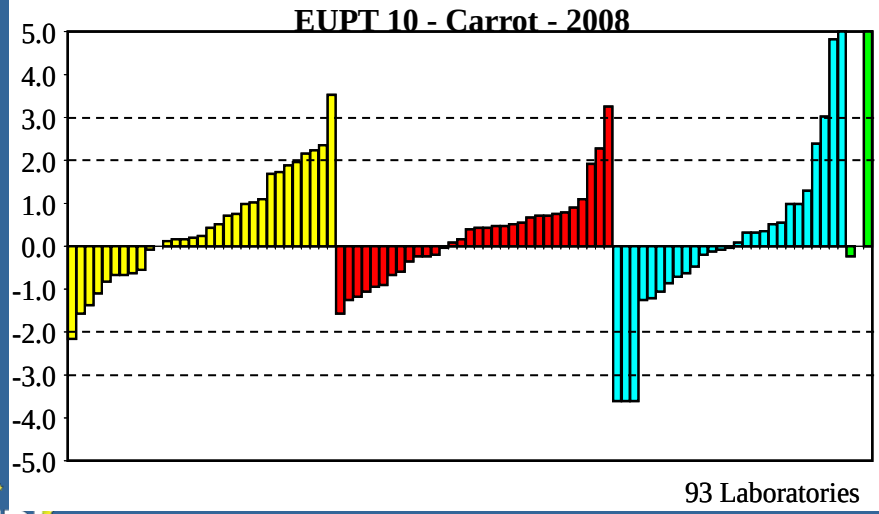
91 Laboratories

Acetone
Acetonitrile
Ethyl Acetate
Methanol

Endosulfan



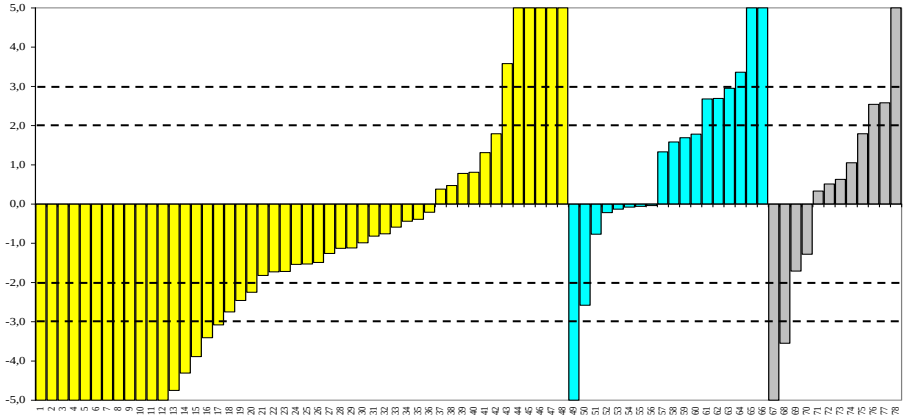




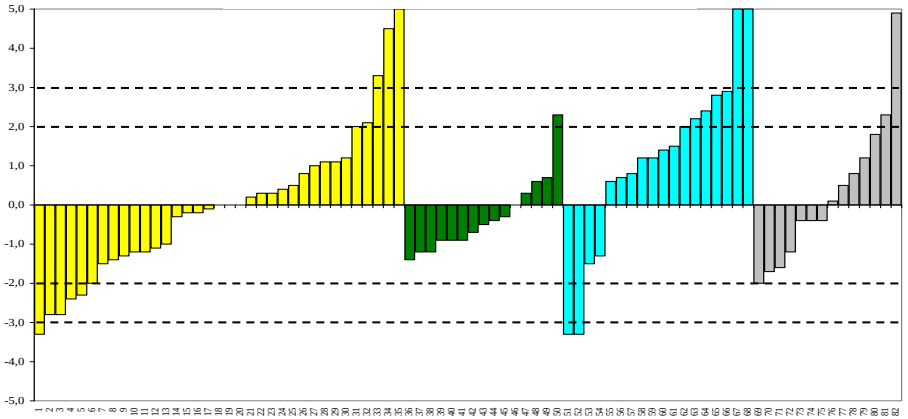
Acetone
Acetonitrile
Ethyl Acetate
Methanol

Methamidophos

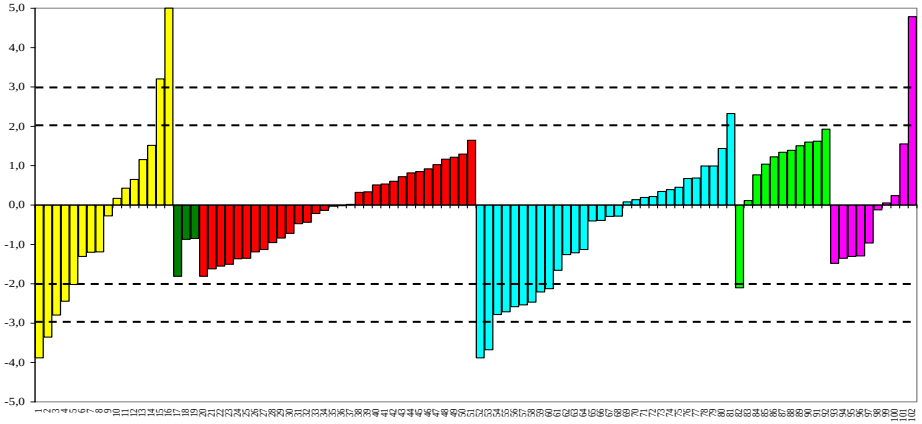
EUPT 1 - Pepper - 1996



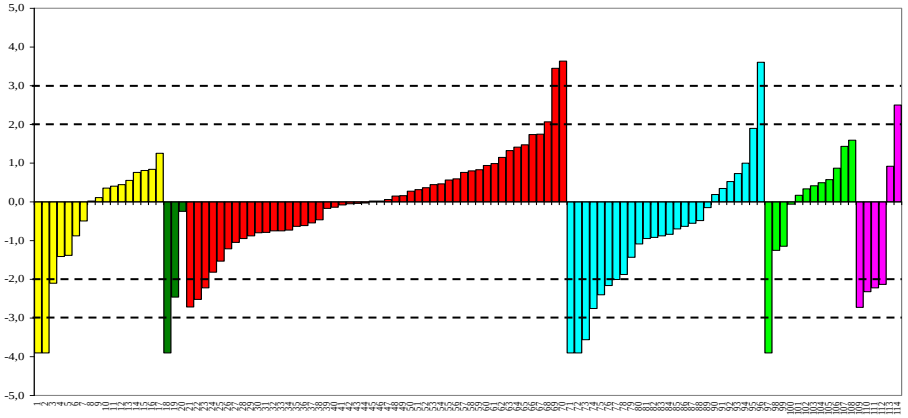
EUPT 3 - Cucumber - 1999



EUPT 10 - Carrot - 2008



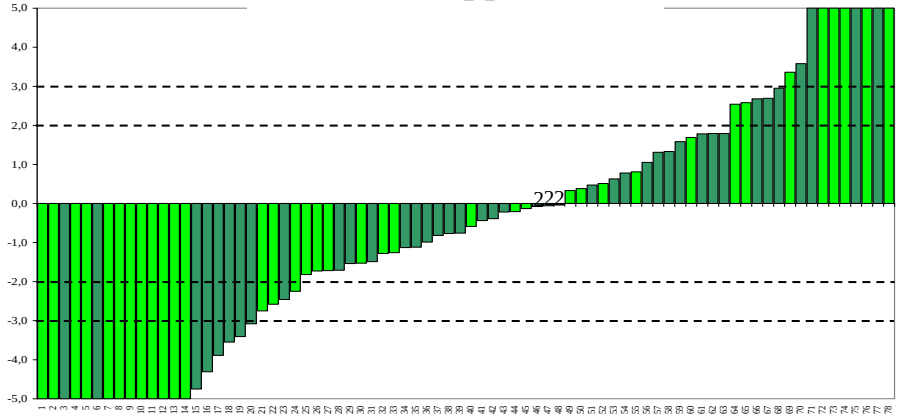
EUPT 11 - Cauliflower - 2009



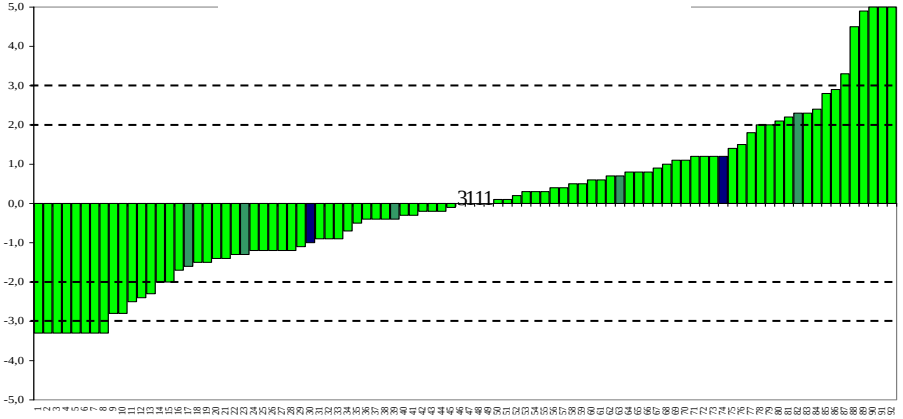
Acetone Acetonitrile Methanol Others
S-19 Ethyl Acetate Dichloromethane

Methamidophos

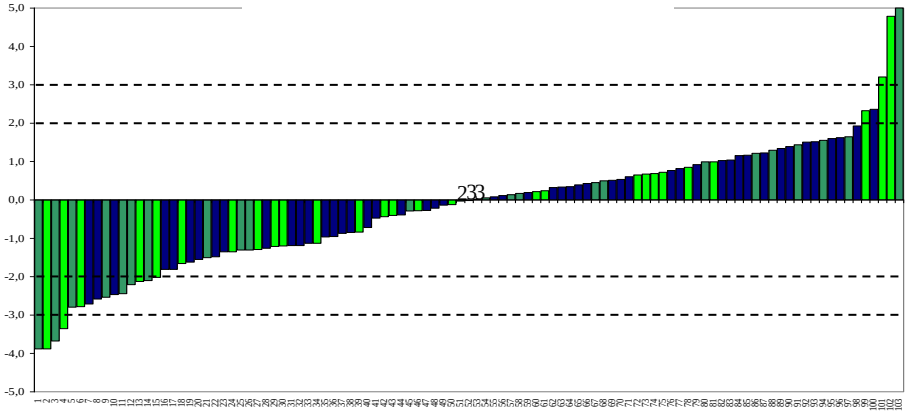
EUPT 1 - Pepper - 1996



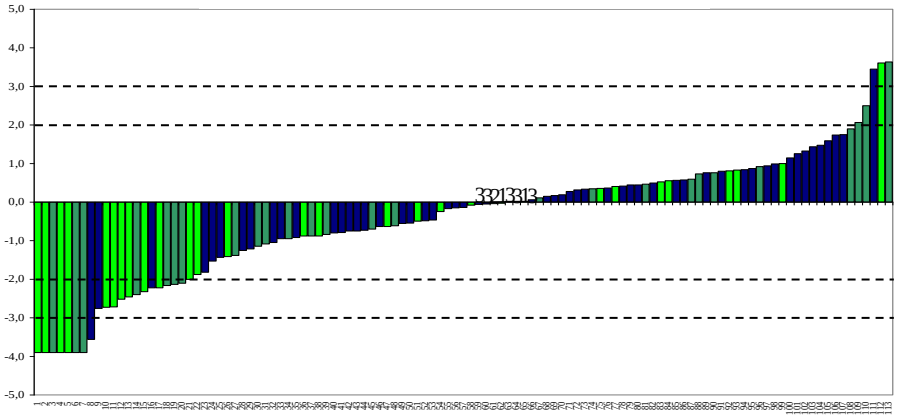
EUPT 3 - Cucumber - 1999



EUPT 10 - Carrot - 2008



EUPT 11 - Cauliflower - 2009



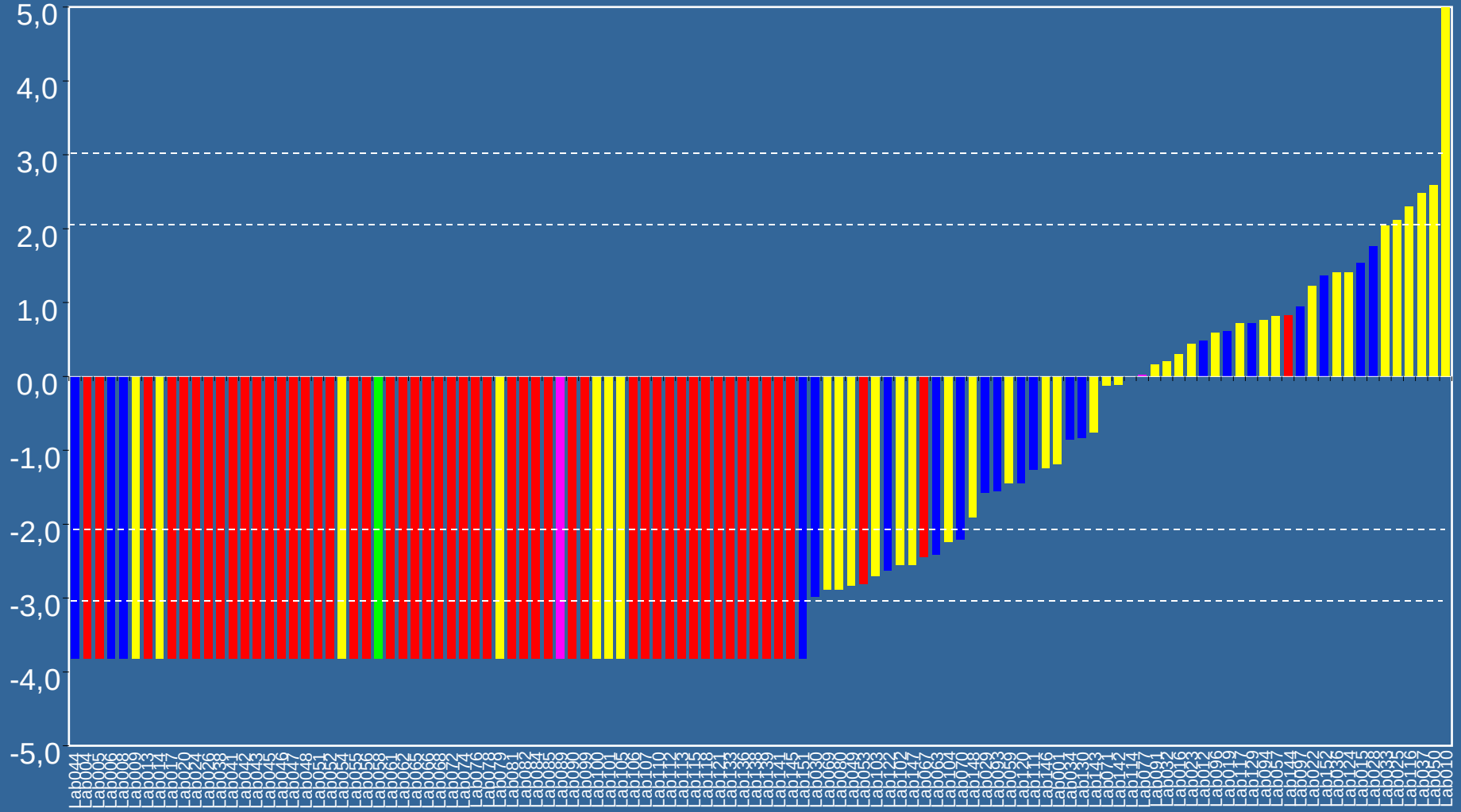
or 1 GC with classical detectors

or 2 GC with MSD

or 3 LC with MSD

Chlorothalonil - EUPT12 - Leeks

Poster PA66



Paula Medina Pastor
10th May 2011

The Reporting of Results

Pesticide Residue Definition needed to be followed

Carbofuran

Pesticide Residue Definition	MRRL
Carbofuran (sum of carbofuran and 3-hydroxy-carbofuran expressed as carbofuran)	0.01
Carbofuran	x
3-hydroxy-carbofuran	x

Correction Factor

Pesticide	Carbofuran Sum	Carbofuran	3-hydroxy-carbofuran
Median (mg/kg)	0.278	0.227	0.055

Carbofuran Sum = $C_{Carbofuran} + 0.933 * C_{3\text{-}OH\text{-}carbofuran}$

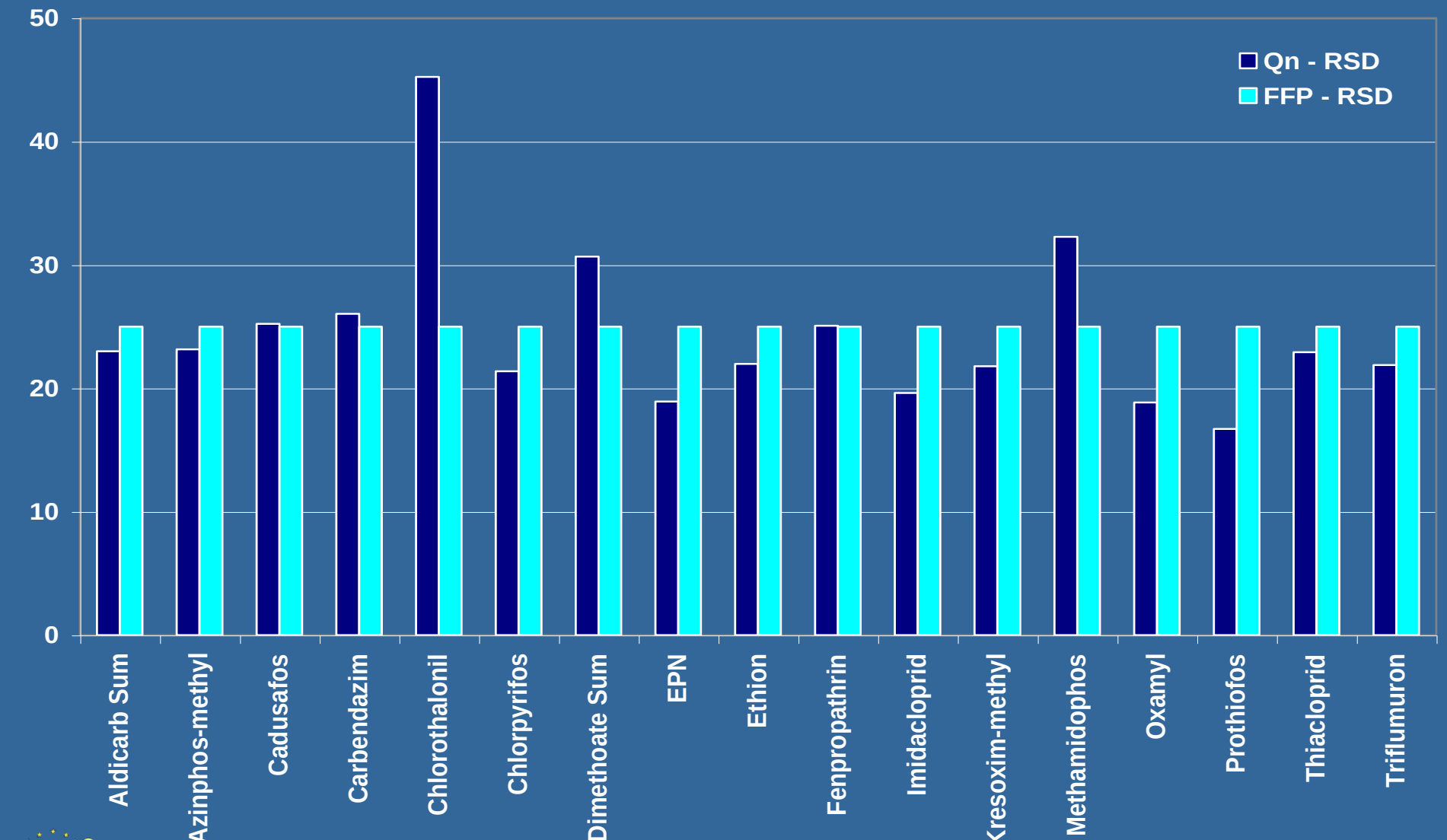
Correct

Lab No.	Carbofuran (sum)	Teoric	Carbofuran	3-hydroxy-carbofuran
Lab106	0.234	0.234	0.183	0.055
Lab107	0.261	0.261	0.21	0.0547
Lab108	0.28	0.277	0.238	0.0415
Lab109	0.252	0.252	0.208	0.0469

Not Correct

Lab No.	Carbofuran (sum)	Teoric	Carbofuran	3-hydroxy-carbofuran
lab121	0.216	0.212	0.154	0.062
lab133	0.241	0.238	0.191	0.05
Lab141	0.311	0.292	0.248	0.047
Lab32	0.222	0.218	0.167	0.0544

The use of FFP-RSD of 25% for all the pesticides



Should the FFP-RSD = 25% be used???

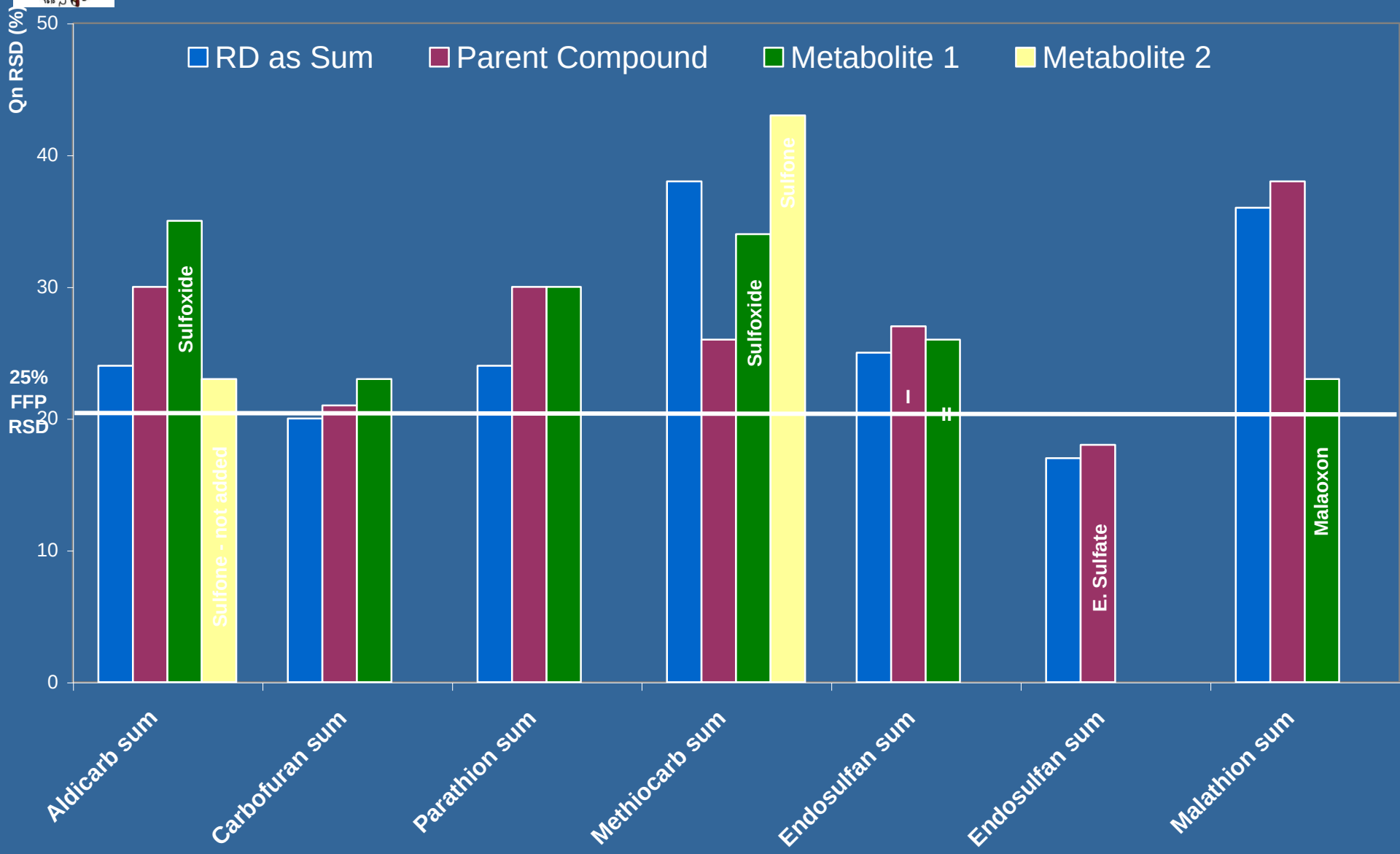
Residue Definition = Σ(Parent Concentration + Metabolite Concentration)

$$\sigma^2_{x+y} = \sigma^2_x + \sigma^2_y$$

$$\sigma_{x+y} = \sqrt{2}\sigma_{x+y} = \sqrt{2} \times 0.25 = 0.35$$

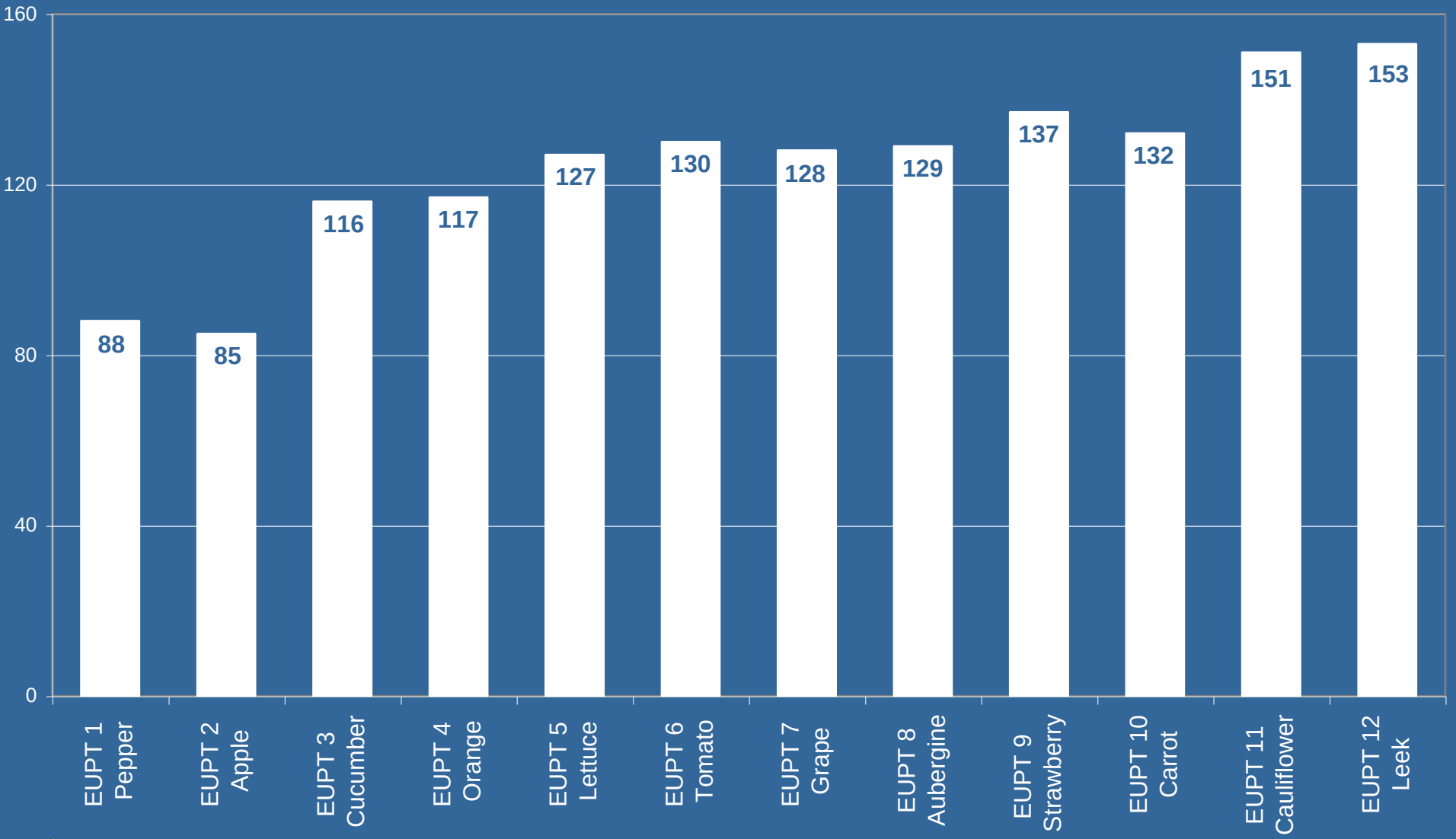
For 3 concentrations

$$\sigma_{x+y+z} = \sqrt{3}\sigma_{x+y+z} = \sqrt{3} \times 0.25 = 0.45$$


Qn RSD (%)
50
40
30
20
10
0
RD as Sum
Parent Compound
Metabolite 1
Metabolite 2
25%
FFP
RSD
Sulfoxide
Sulfone - not added
Sulfoxide
Sulfone
I
II
E. Sulfate
Malaoxon
Aldicarb sum
Carbofuran sum
Parathion sum
Methiocarb sum
Endosulfan sum
Endosulfan sum
Malathion sum

The Participation

Number of Official Labs Participating



Country	No. of Labs	Country	No. of Labs
Austria	1	Latvia	1
Belgium	4	Lithuania	1
Bulgaria	6	Luxemburg	1
Cyprus	1	Malta	1
Czech Republic	2	Norway	1
Denmark	2	Poland	14
Estonia	2	Portugal	3
Finland	2	Romania	2
France	6	Slovakia	1
Germany	23	Slovenia	3
Greece	9	Spain	14
Hungary	6	Sweden	2
Iceland	1	Switzerland	3
Ireland	1	The Netherlands	2
Italy	20	United Kingdom	4

EU and EFTA Countries Participation

Other Countries

Country
Brazil
Egypt
Singapore
Turkey
Uruguay

Conclusions:

The European Proficiency Tests in Fruits and Vegetables are a useful tool to evaluate the analytical capability of the official laboratory. It is evaluated:

- **their scope**
- **their accuracy**
- **additional information on:**
  - *** low concentration**
  - *** evaluation of individual compounds**

I would like to thank my group for the work done in every EUPT-FV conducted!!!

MUCHAS GRACIAS POR SU ATENCIÓN!!!!

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