EUPT-SRM5 Pesticide Residues in Apple Purée

(in cooperation with EURL-FV)

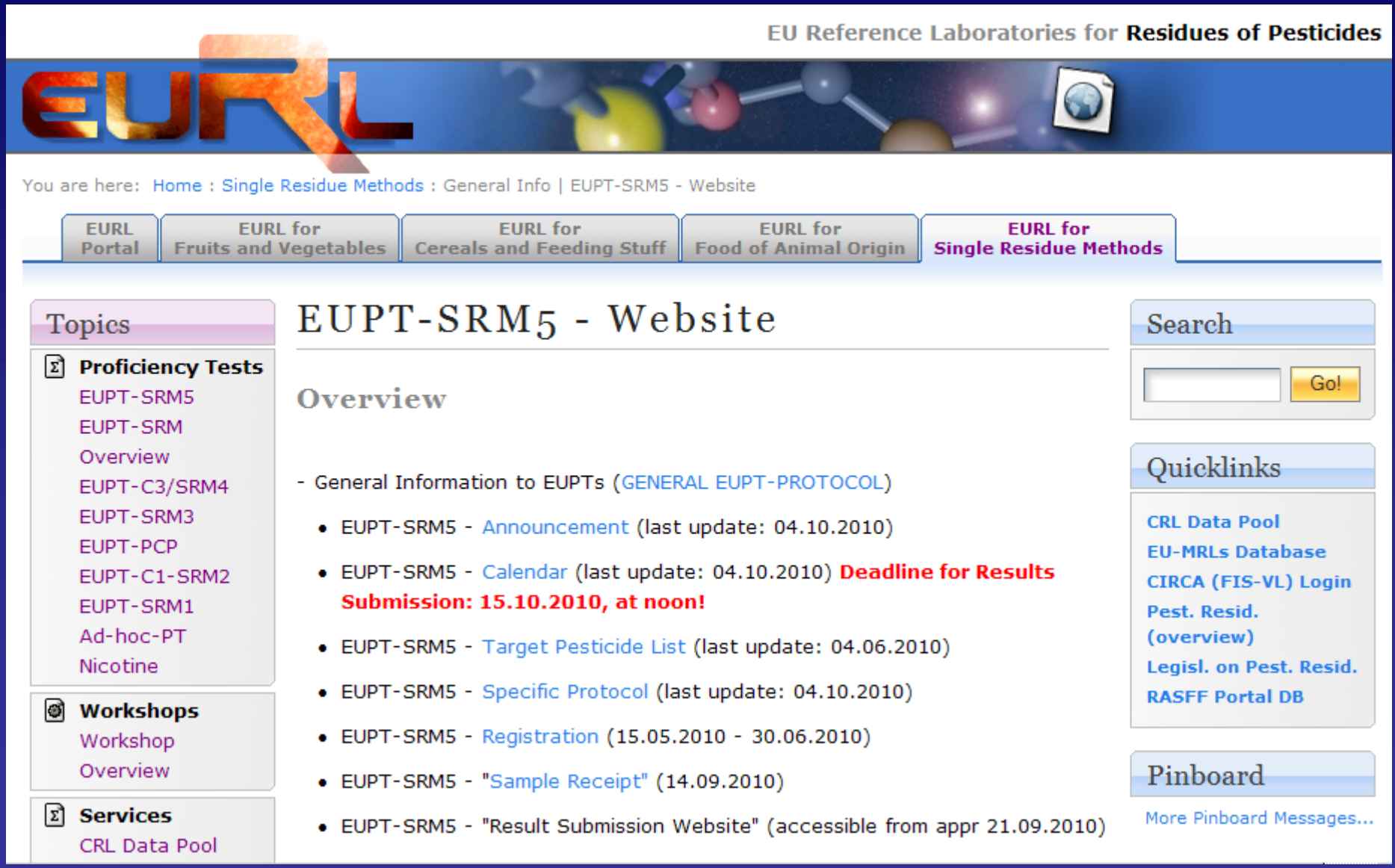
PRELIMINARY RESULTS

EUPT-SRM5 on Apple Purée September/October 2010

Homogeneity and Stability

Compound	Stability Test	Homogeneity test	Sample portion [g]
Fluazifop	passed	passed	10
Ethephon	passed	passed	10
Dithiocarbamates	passed	passed	10
Abamectin	passed	passed	10
Fenbutatin oxide	passed	passed	10

EUPT-SRM5 on Apple Purée September/October 2010



EUPT-SRM5 on Apple Purée September/October 2010

Announcement

EU Reference Laboratories for F

EURL

You are here: Home : Single Residue Methods : General Info | EUPT-SRM5 - Announcement

EURL Portal | EURL for Fruits and Vegetables | EURL for Cereals and Feeding Stuff | EURL for Food of Animal Origin | EURL for Single Residue Metho

Topics

Proficiency Tests
- EUPT-SRM5
- EUPT-SRM
- Overview
- EUPT-C3/SRM4
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- EUPT-PCP
- EUPT-C1-SRM2
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Library

EUPT-SRM5 - Announcement

Dear Colleagues,

We herewith cordially invite you to participate in the upcoming European Proficiency Test on the determination of pesticide residues using single residue methods (EUPT-SRM5). This test is organised by the EU Reference Laboratory for pesticides using Single Residue Methods (EURL-SRM) in collaboration with the EURL for pesticides in Fruit and Vegetables (EURL-FV).

The test material for EUPT-SRM5 is **apple sauce** (apple purée).

Eligible labs for this test are all Official Laboratories (OLs) analysing pesticide residues in fruits and vegetables as well as all National Reference Laboratories (NRLs) for pesticide residues using single residue methods.

Please note that **participation is mandatory for all eligible labs** (see Art. 28 Regulation (EC) No 396/2005).

Eligible labs that do not intend to participate in this test (e.g. because none of the pesticides in the target list is within the lab's scope, or for other reasons) are expected by the Commission, on behalf of which this proficiency test is undertaken, to **state the reasons for non-participation**. These reasons should **be reported on the "EUPT-Registration Website"**.

To register for this PT please access the "EUPT-Registration Website". This

Search

Go!

Quicklinks

- CRL Data Pool
- EU-MRLs Database
- CIRCA (FIS-VL) Login
- Pest. Resid. (overview)
- Legisl. on Pest. Resid.
- RASFF Portal DB

Pinboard

More Pinboard Messages...

EUPT-SRM5 on Apple Purée September/October 2010

Calendar

EU Reference Laboratories for **Residues of Pesticides**

Single Residue Methods

CALENDAR for the EUPT – SRM5

(last update 04.10.2010)

Activity	Who ?	Dates
Opening of the **EUPT-SRM5 Website** with further information including links to "**Announcement/Invitation-Letter**", "**Calendar**", "**Target Pesticide List**", "**General Protocol**",	EURL-SRM	Feb 2010
Invitation to laboratories to participate	EURL-SRM	11 May 2010
Release of Specific Protocol	EURL-SRM	15 May 2010
Access to "**EUPT-Registration Website**"	EURL-SRM (in collaboration with EURL-CF)	**15 May 2010**
Deadline for registration	Invited Labs	**30 Jun 2010**
Preparation of Test Material	EURL-FV (on behalf of EURL-SRM)	July 2010 (pre-tests) Sep 2010 (final preparation)
Homogeneity tests	EURL-SRM	Sep 2010
Stability tests	EURL-SRM	Sep-Oct 2010
▪ **Distribution of Test materials** ▪ Information to the laboratories regarding shipment	EURL-FV (on behalf of EURL-SRM)	**13 Sep 2010**
Activation of "**EUPT-SRM5 Result Submission Website**"	EURL-SRM	**by 14 Sep 2010**
Deadline for Receipt and Acceptance of Test Materials: Online Submission of Form 0 (sub-page 0)	Participating Labs	**within 48 hr of receipt**
Deadline for Result Submission **Pesticide scope, Results, Method Information** Submission of Form 1 – 3 (sub-pages 1 – 3)	Participating Labs	**by 15 Oct 2010**
EUPT Evaluation Meeting	EURL-FV, EURL-SRM, Commission, EUPT-Scientific Committee	Oct/Nov 2010

EUPT-SRM5 on Apple Purée September/October 2010

Possible Pesticide List for SRM

EU Reference Laboratories for **Residues of Pesticides**

CRL

Single Residue Methods

TARGET PESTICIDE LIST FOR THE EUPT – SRM5

(last updated: 04.06.2010)

Pesticides marked with an asterisk "*" will be considered in the overall performance-ranking of the labs. This concerns both the inclusion of those compounds in the scope of the labs as well as the results (z-scores) achieved by the labs for the compounds present in the sample.

Pesticides	Residue Definitions (valid within this EUPT)	MRRL (mg/kg)	Considered in overall performance-ranking	Included in EU CCP 2010?
ACIDIC PESTICIDES				
*2,4-D	2,4-D (free acid only)	0.01	Yes	Yes
*Fluazifop	Fluazifop (free acid only)	0.01	Yes	Yes
*Haloxyfop	Haloxyfop (free acid only)	0.01	Yes	Yes
Dichlorprop (2,4-DP)	Dichlorprop (free acid only)	0.01	No	No
HIGHLY POLAR PESTICIDES				
*Chlormequat	Chlormequat (free cation)	0.01	Yes	Yes
*Ethephon	Ethephon	0.02	Yes	Yes
*Mepiquat	Mepiquat (free cation)	0.01	Yes	Yes
Amitrole	Amitrole	0.02	No	Yes
OTHER CCP RELATED PESTICIDES				
*Dithiocarbamates	Dithiocarbamates expressed as CS_2 (including maneb, mancozeb, meti-ram, propineb, thiram and ziram)	0.02	Yes	Yes
*Abamectin	Avermectin B1a only	0.01	Yes	Yes
*Fenbutatin oxide	Fenbutatin oxide	0.01	Yes	Yes

EUPT-SRM5 on Apple Purée September/October 2010

Preparation and Shipment of Test materials I

EUPT-SRM5 on Apple Purée September/October 2010

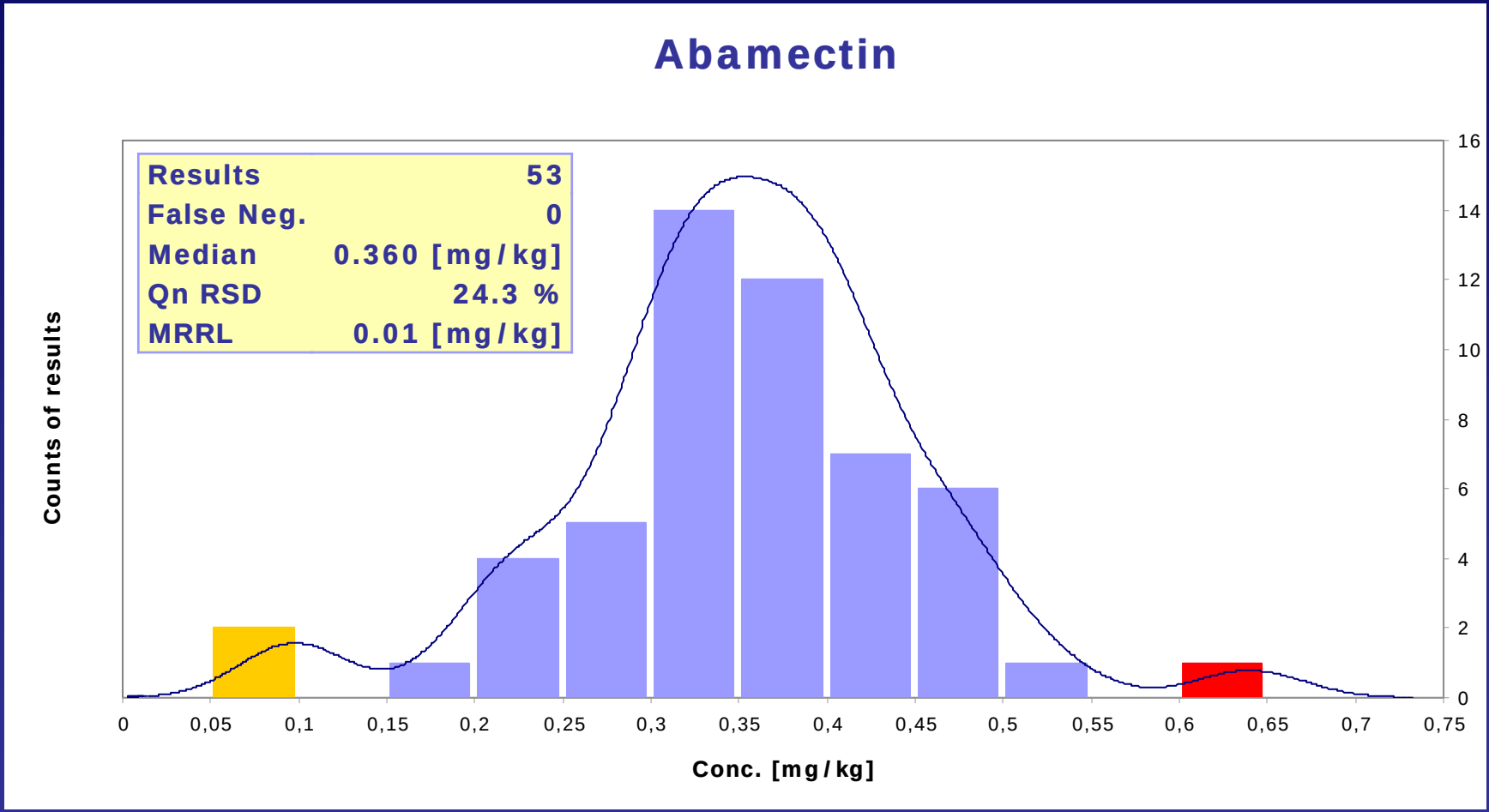
Preparation and Shipment of Test materials II

EUPT-SRM5 on Apple Purée September/October 2010

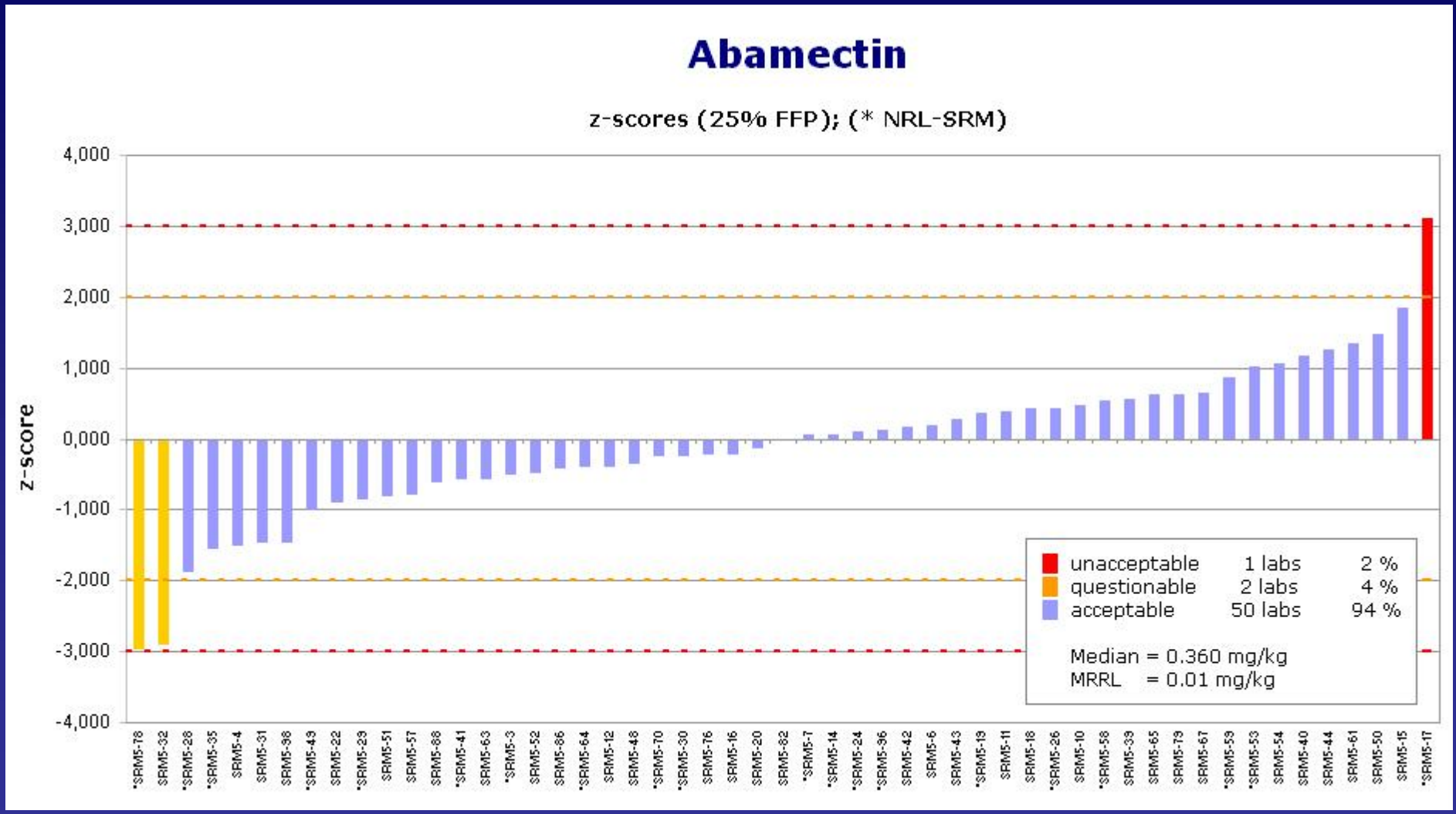
Participating Labs / Countries

Country	Registered		Submitting Results		Notes
	Labs	NRL-SRM	Labs	NRL-SRM	
Austria	1	1	1	1	
Belgium	4	1	4	1	
Bulgaria	1	1	1	1	
Cyprus	1	1	1	1	
Czech Republic	2	1	2	1	
Denmark	2	1	2	1	
Estonia	2	1	2	1	
Finland	1	1	1	1	
France	6		6		No NRL-SRM officially established
Germany	13	1	13	1	
Greece	4	2	4	2	
Hungary	3	1	3	1	
Ireland	1	1	1	1	
Italy	8	1	5	1	
Latvia	1	1	1	1	
Lithuania	1	1	1	1	
Malta	1	(1)	1	(1)	Represented by NRL-SRM of UK
Poland	10	1	9	1	
Portugal	4	1	4	1	
Slovakia	1	1	1	1	
Slovenia	3	1	3	1	
Spain	8	1	6	1	
Sweden	1	1*	1	1*	*Proxy
The Netherlands	1	1	1	1	
UK	4	1	3	1	
EU Sum	**85**	**24**	**78**	**24**	
Croatia	1				
Egypt	1		1		
Norway	1	1	1	1	
Switzerland	1		1		
Overall Sum	**89**	**25**	**81**	**25**	

EUPT-SRM5 on Apple Purée September/October 2010



EUPT-SRM5 on Apple Purée September/October 2010



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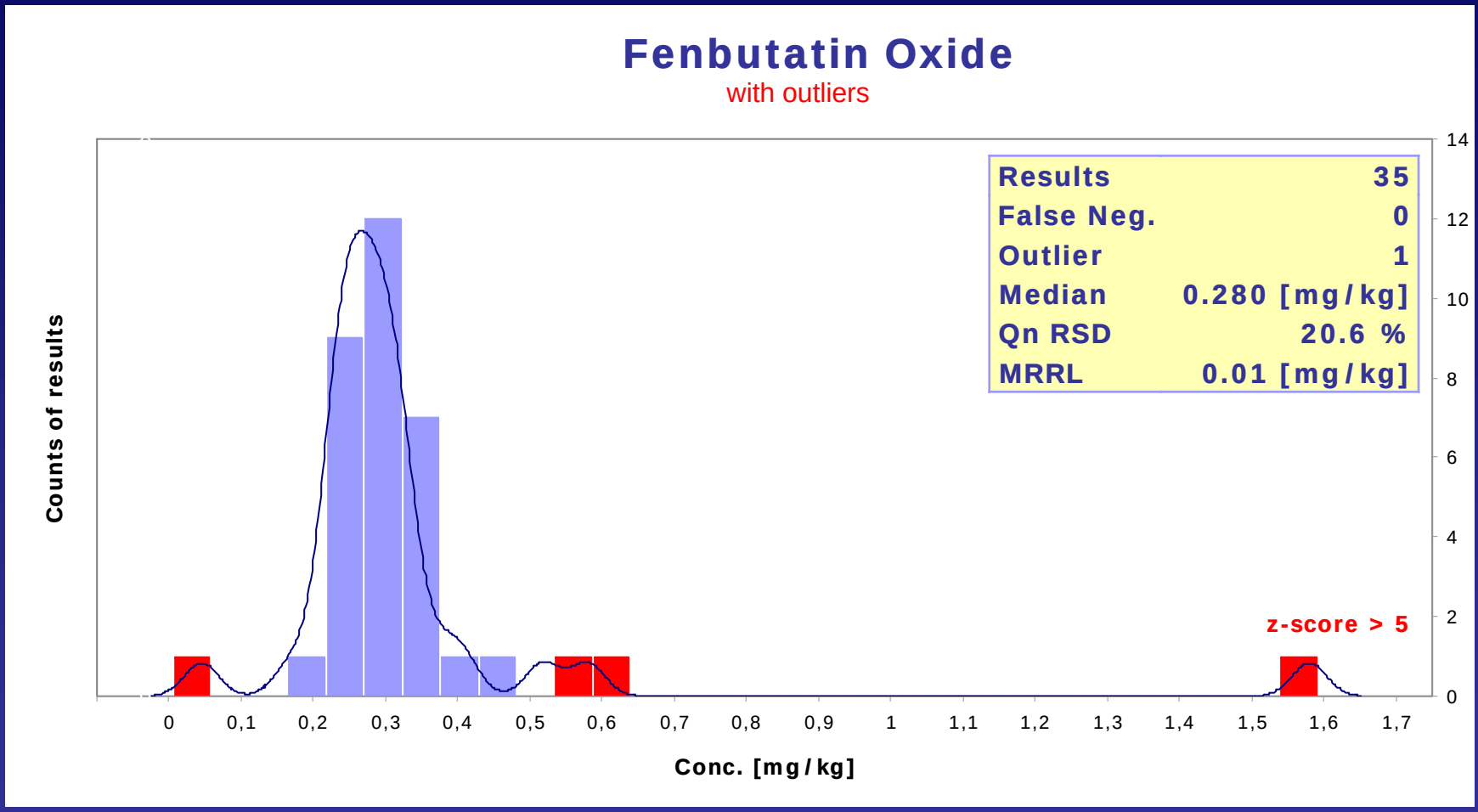

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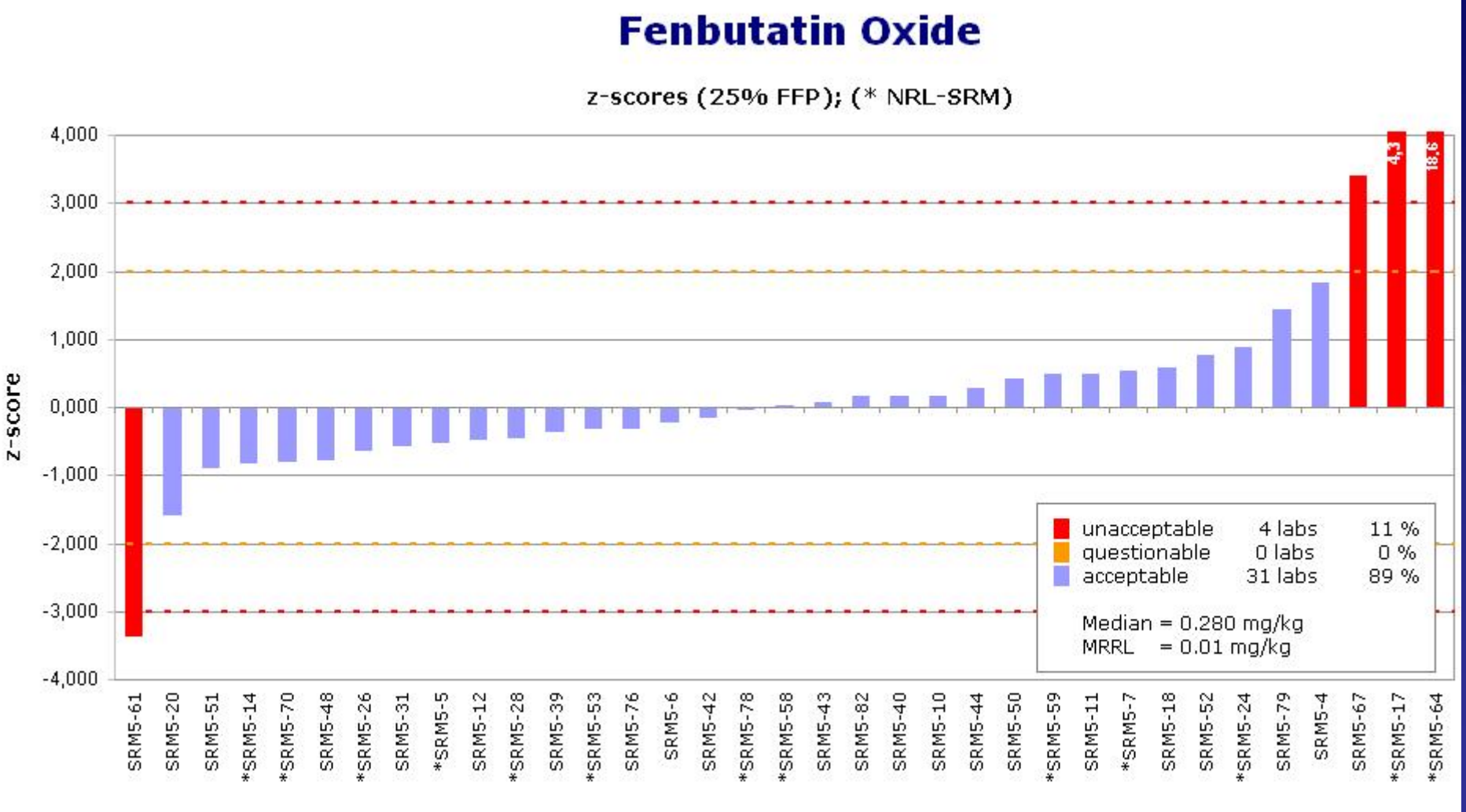

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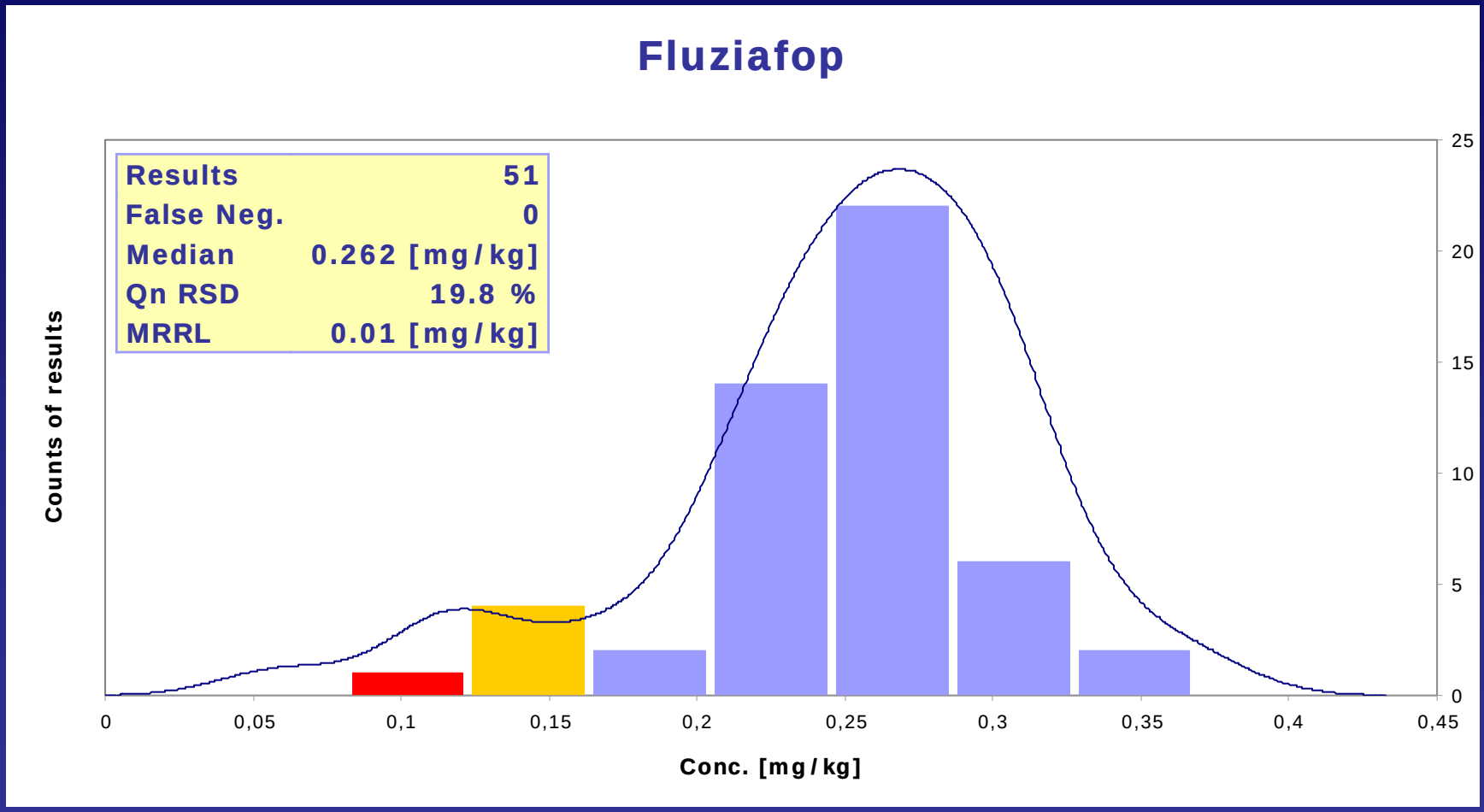

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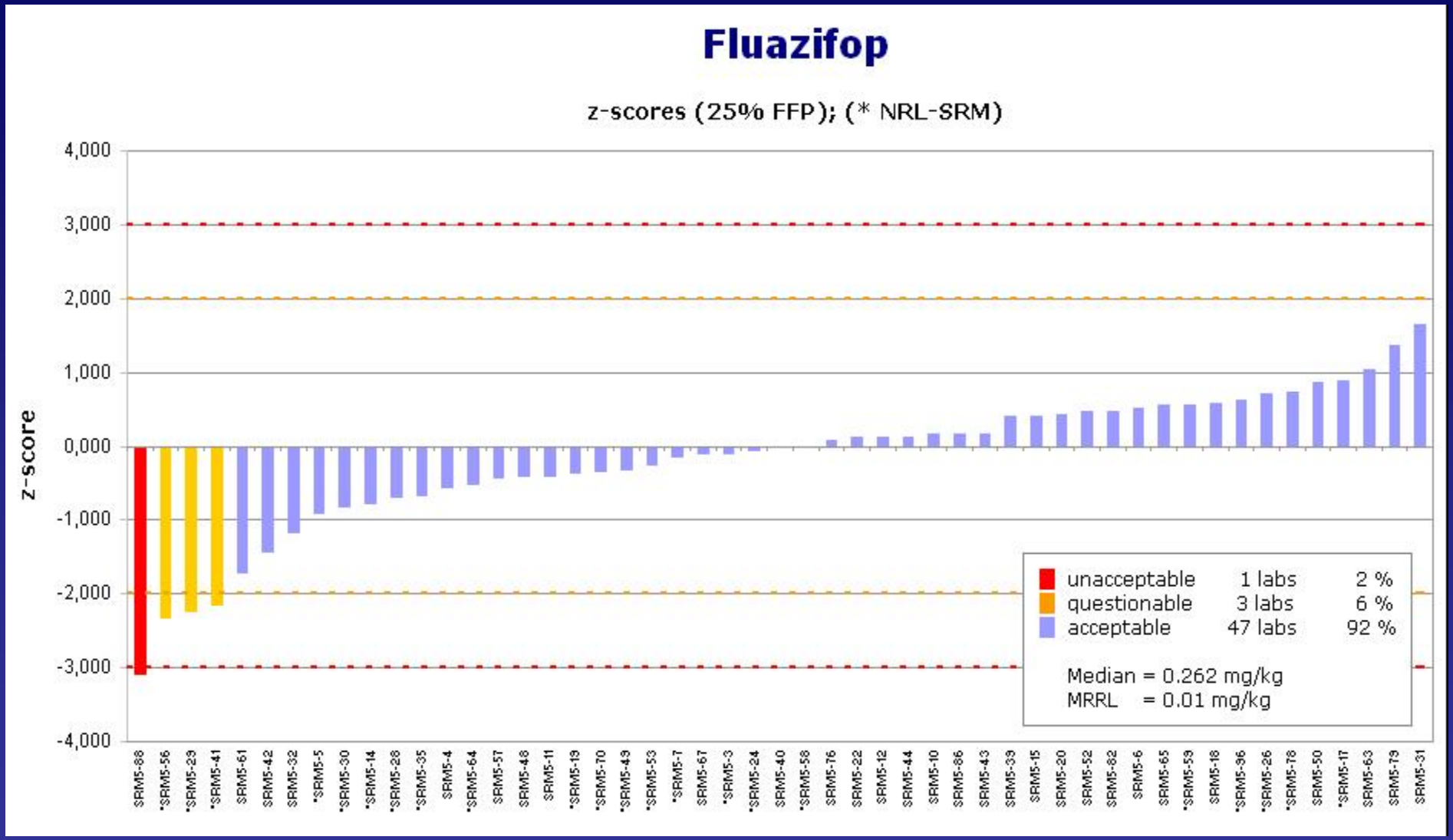

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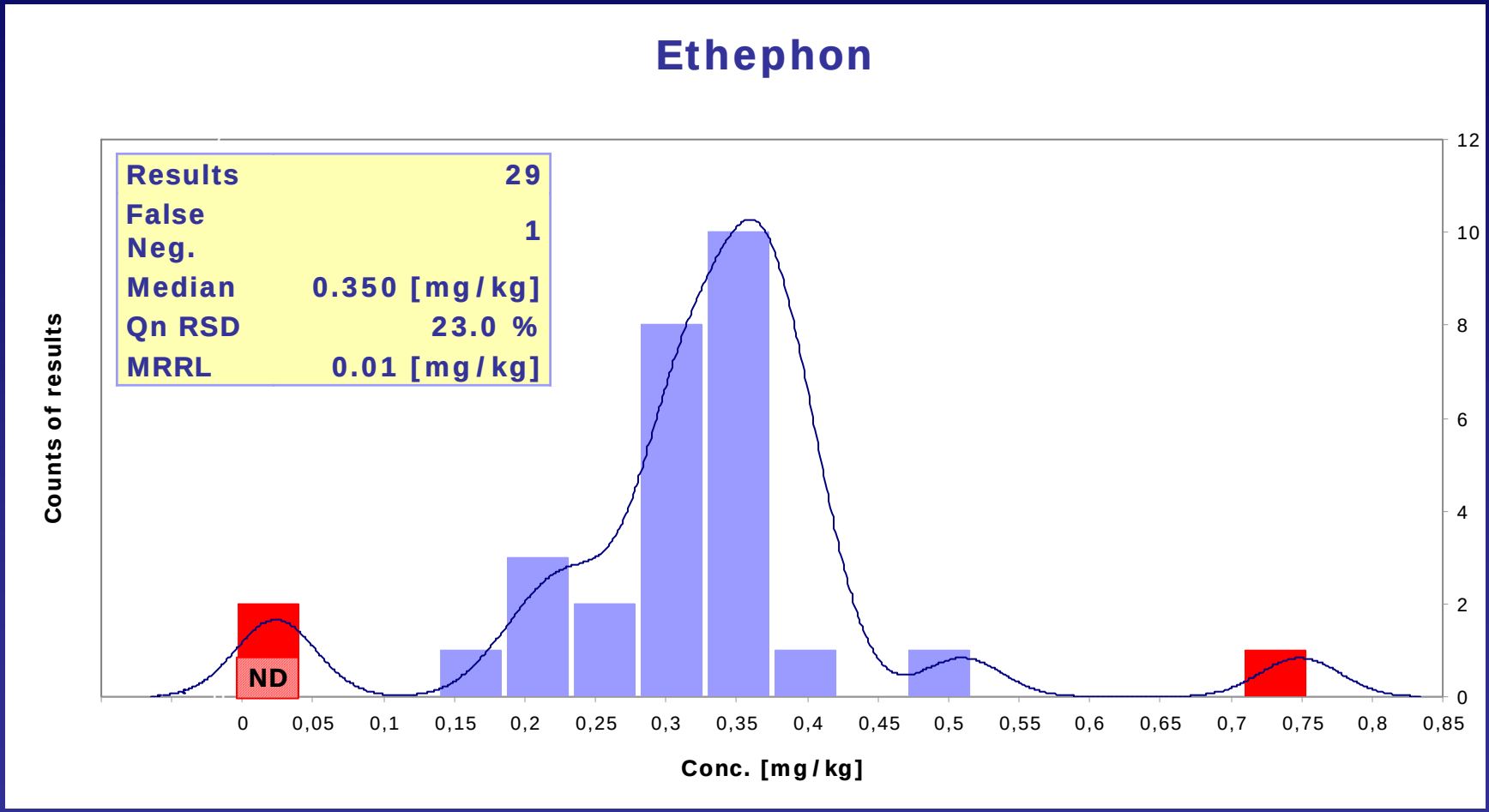

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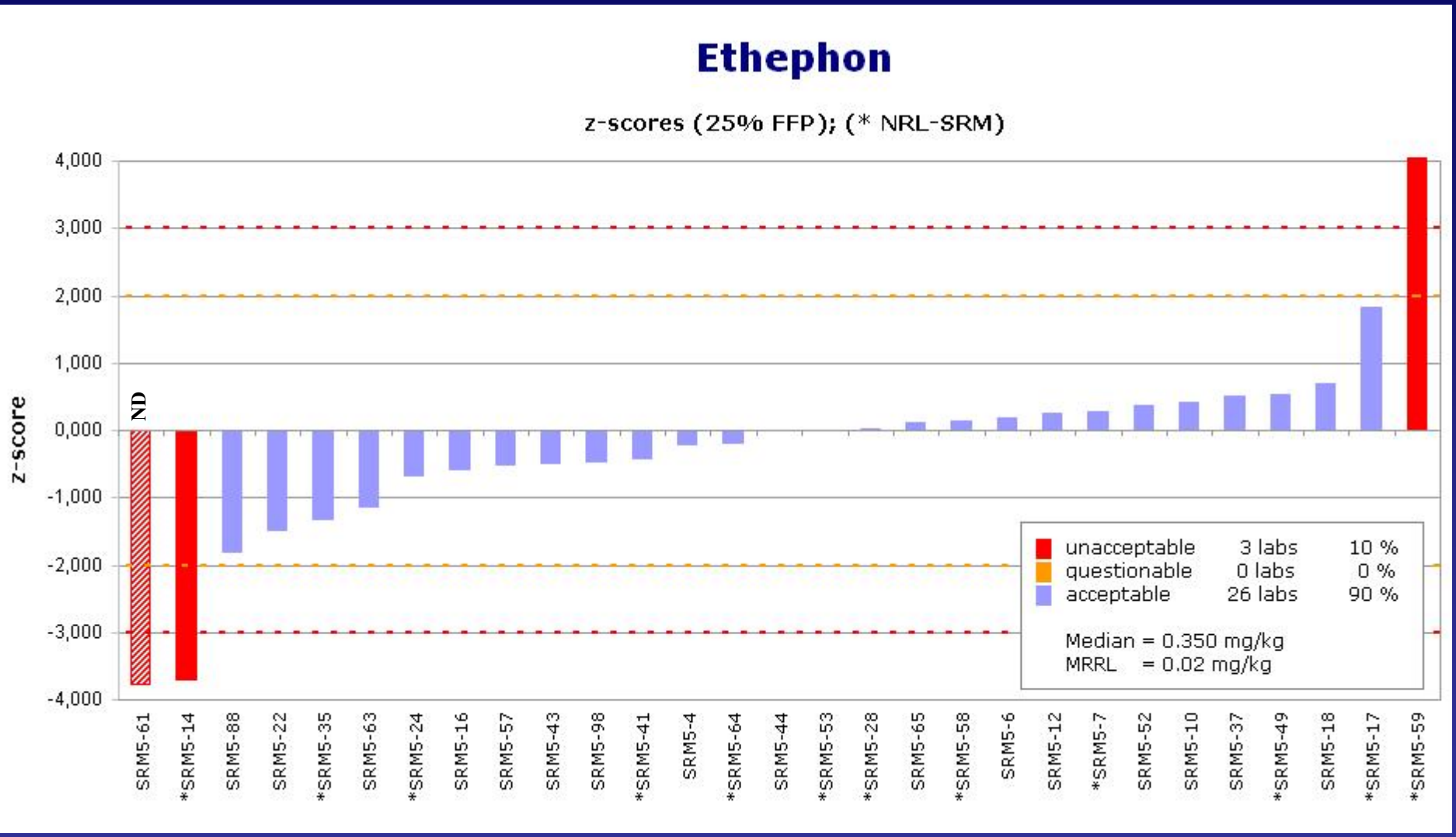

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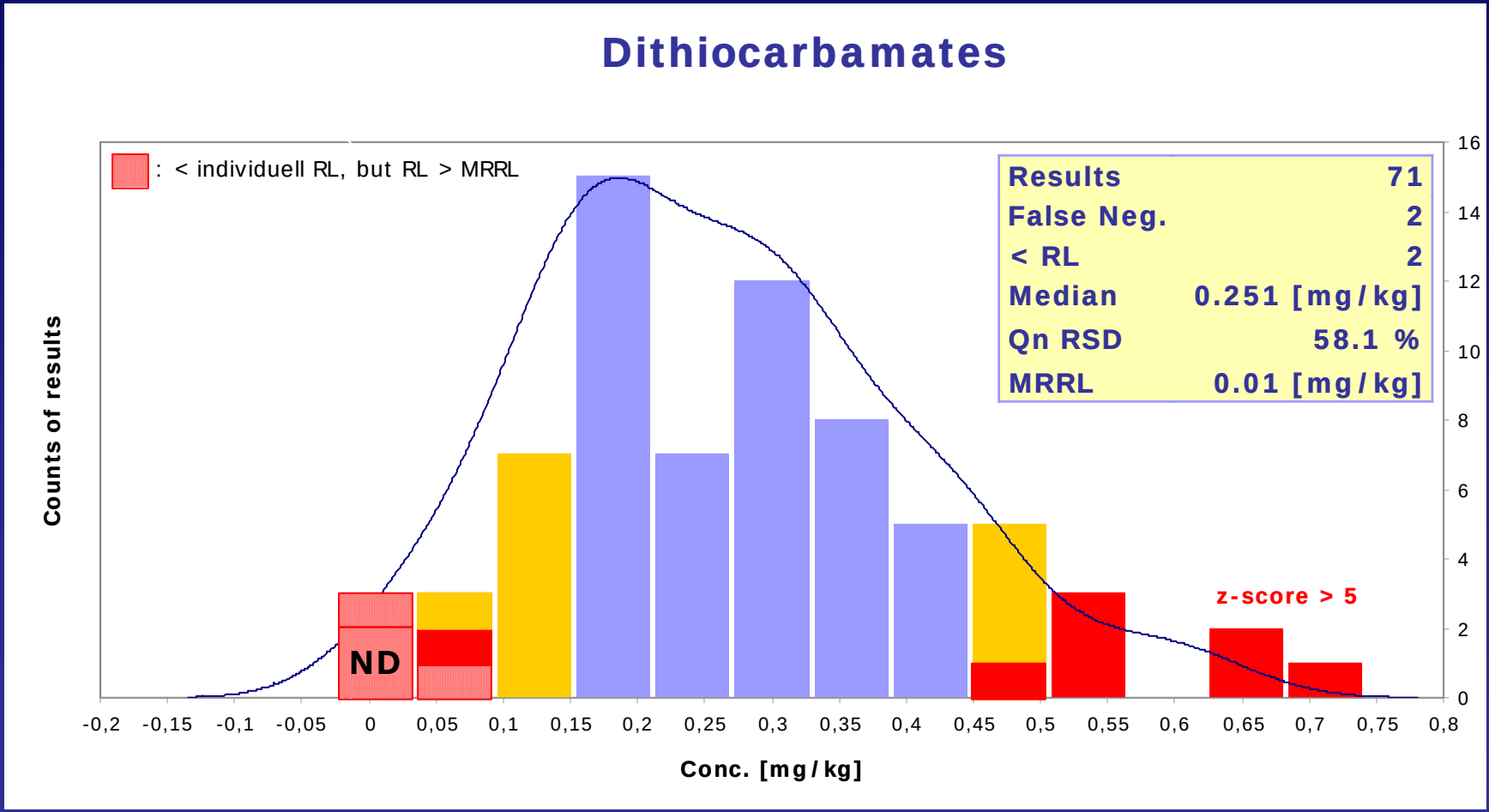

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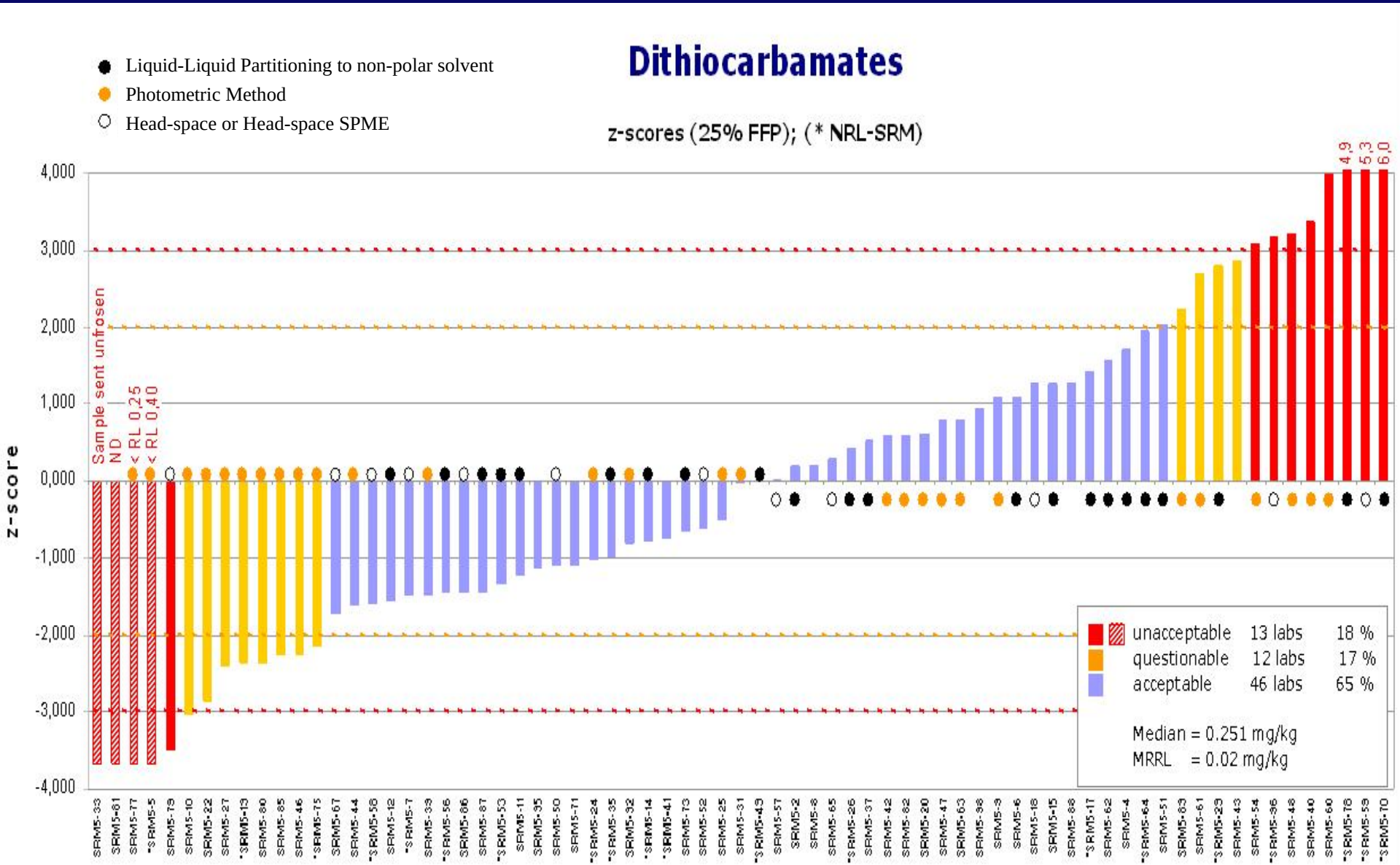


EUPT-SRM5 on Apple Purée September/October 2010

Dithiocarbamates – Evaluation by Method

Method of Detection	No. of Labs	false Neg	Median* mg/kg	Qn RSD [%]	☺ A	😐 Q	☹ U
LLP-GC (isooctane)	22		0.281	39.7	**18 (80 %)**	2 (10 %)	**2 (10 %)**
Photometric	28	2 #	0.235	70.3	**12 (43 %)**	9 (32 %)	**7 (25 %)**
Headspace - GC Headspace SPME - GC	12		0.171	60.2	**9 (75 %)**	0 (0 %)	**3 (25 %)**
Not indicated	9	2	0.264	71.2	**6 (67 %)**	1 (11 %)	**2 (22 %)**
DTCs OVERALL	**71**	**2+2 #**	**0.251**	**58.1**	**46 (65%)**	**12 (17%)**	**13 (18%)**

*: Excluding |z|-score > 5 and false negatives

#: "< RL", while RL > MRRL and > assigned value

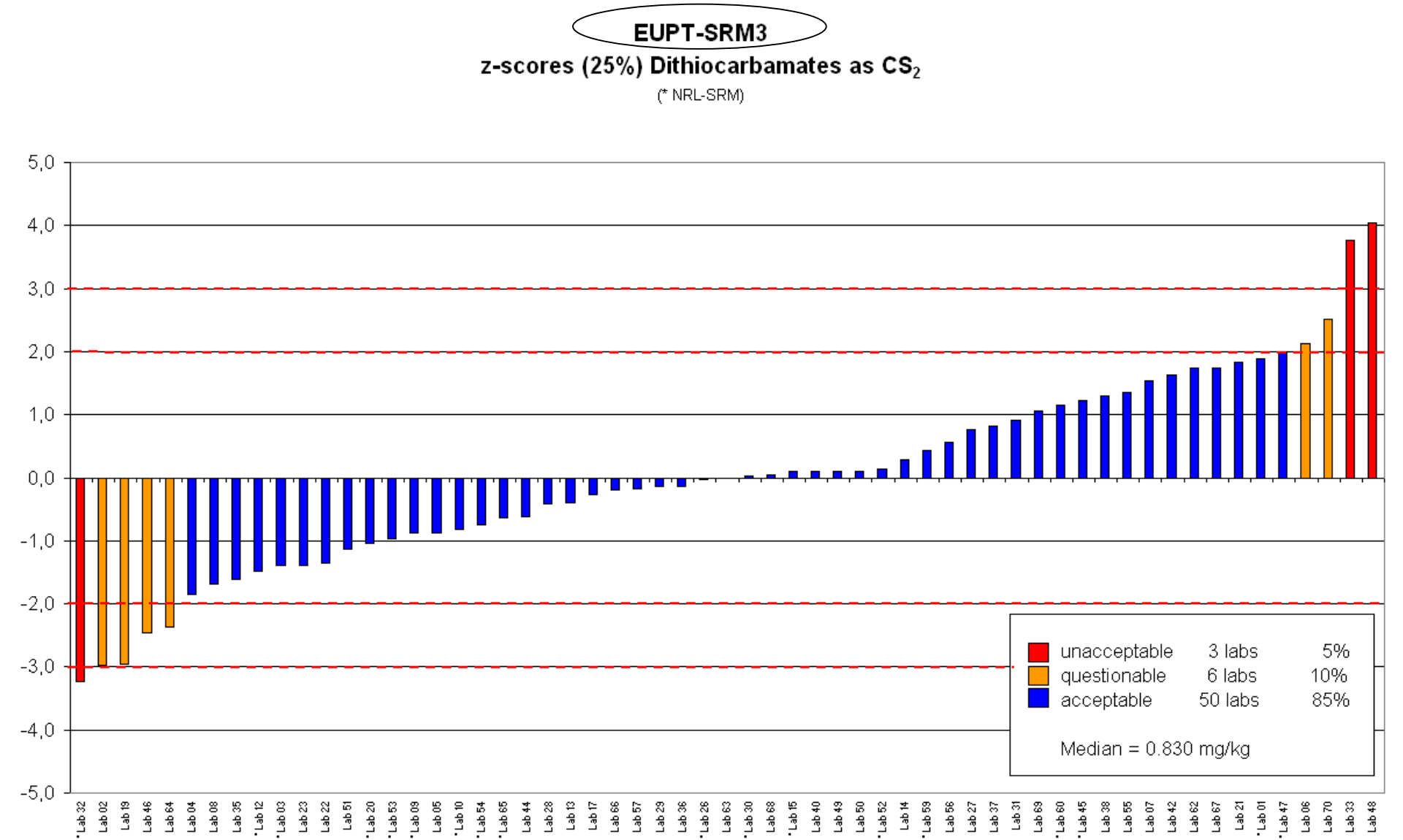
A: Acceptable;
Q: Questionable;
U: Unacceptable

Comparison of PTs

Dithiocarbamates

	SRM 3 (2008)	SRM 5 (2010)
Commodity	Carrot Homogenate	Apple Purée
No. of Results / false Neg.	59 / 0	71 / 4
MRRL [mg/kg]	0.05	0.02
Qn RSD [%]	38	58
Acceptable (FFP RSD 25 %)	85 %	65 %
Assigned Value [mg/kg]	0.762	0.251

EUPT-SRM5 on Apple Purée September/October 2010



Overall Performance I

Compound	No. of Labs	false Neg	Mean* |z|	Qn RSD [%]	☺ A	😐 Q	☹ U
Fluazifop	51		0.69	19.8	**47 (92%)**	3 (6%)	**1 (2%)**
Ethephon	29	1	0.82	23.0	**26 (90%)**	0 (0%)	**3 (10%)**
Dithiocarbamates	71	2+2#	1.60	58.9	**46 (65%)**	12 (17%)	**13 (18%)**
Abamectin	53		0.79	24.3	**50 (94%)**	2 (4%)	**1 (2%)**
Fenbutatin Oxide	35		0.83	20.6	**31 (89%)**	0 (0%)	**4 (11%)**

*: Excluding outliers and false negatives

#: two of them < RL, while RL > MRRL, and one sample sent unfrozen

A: acceptable; Q: questionable; U: unacceptable

Overall Performance II

False Positives

Compounds	No. of Labs
Amitrole	3 (2 x HU, 1x FR)
2,4 – D	1 (IT)
Chlormequat	1 (IT)
Mepiquat	1 (IT)

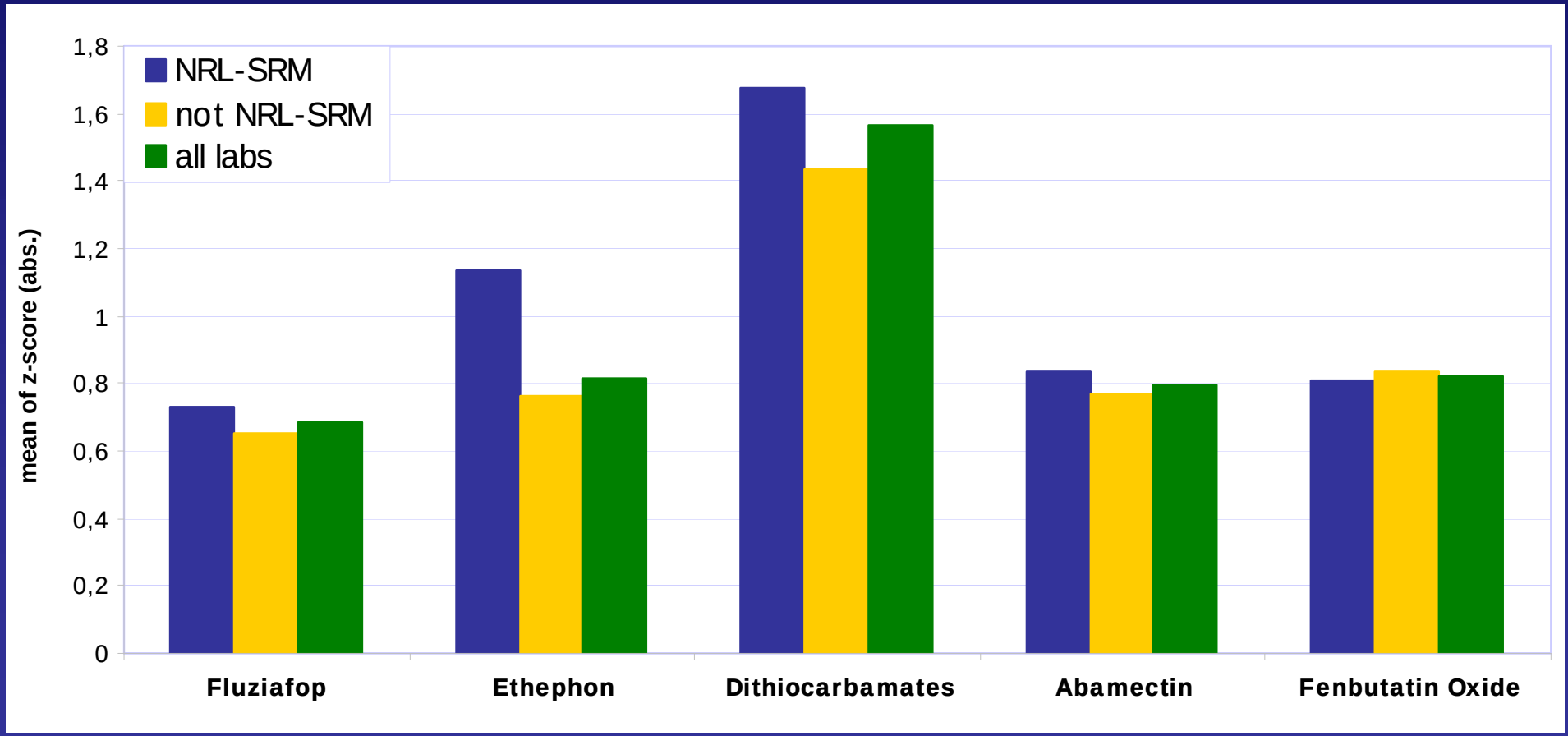
False Negatives

Compounds	No. of Labs
Ethephon	1 (IT)
Dithiocarbamates	2+2 (FR, IT, GR, ES)

EUPT-SRM5 on Apple Purée September/October 2010

NRL-SRMs vs. OfLs

Mean z-score (abs.)



Experience with the Analysis of Compounds

	DTC		Fluazifop		Abamectin		Fenbutatin Oxide		Ethephon	
	No.	%	No.	%	No.	%	No.	%	No.	%
Long (> 2 years)	61	86%	23	45%	21	40%	10	29%	6	21%
Short (1 - 2 years)	1	1%	12	24%	14	26%	4	11%	5	17%
Very short (< 1 year)	1	1%	10	20%	10	19%	12	34%	8	28%
None	0	0%	2	4%	5	9%	9	26%	8	28%
NoData	8	11%	4	8%	3	6%	0	0%	2	7%
TOTAL	71	100%	51	100%	53	100%	35	100%	29	100%

Methods employed

	QuEChERS - Type	EtAc - Type	Luke/S19 - Type	Other	No Data
	% of N				
Fluazifop (N = 51)	X (75%) (2x deriv.)	X (2 %)	X (4 %)	X (19 %) (1x deriv.)	X (x %)
Abamectin (N = 53)	X (74 %)	X (6 %) (1x deriv.)	X (2 %)	X (18 %) (1x deriv.)	4 (x %)
Fenbutatin Oxide (N = 35)	X (80 %)	- (-)	X (3 %)	X (17 %) (2x deriv.)	X (x %)

N = All labs that analysed for a compound

Methods employed

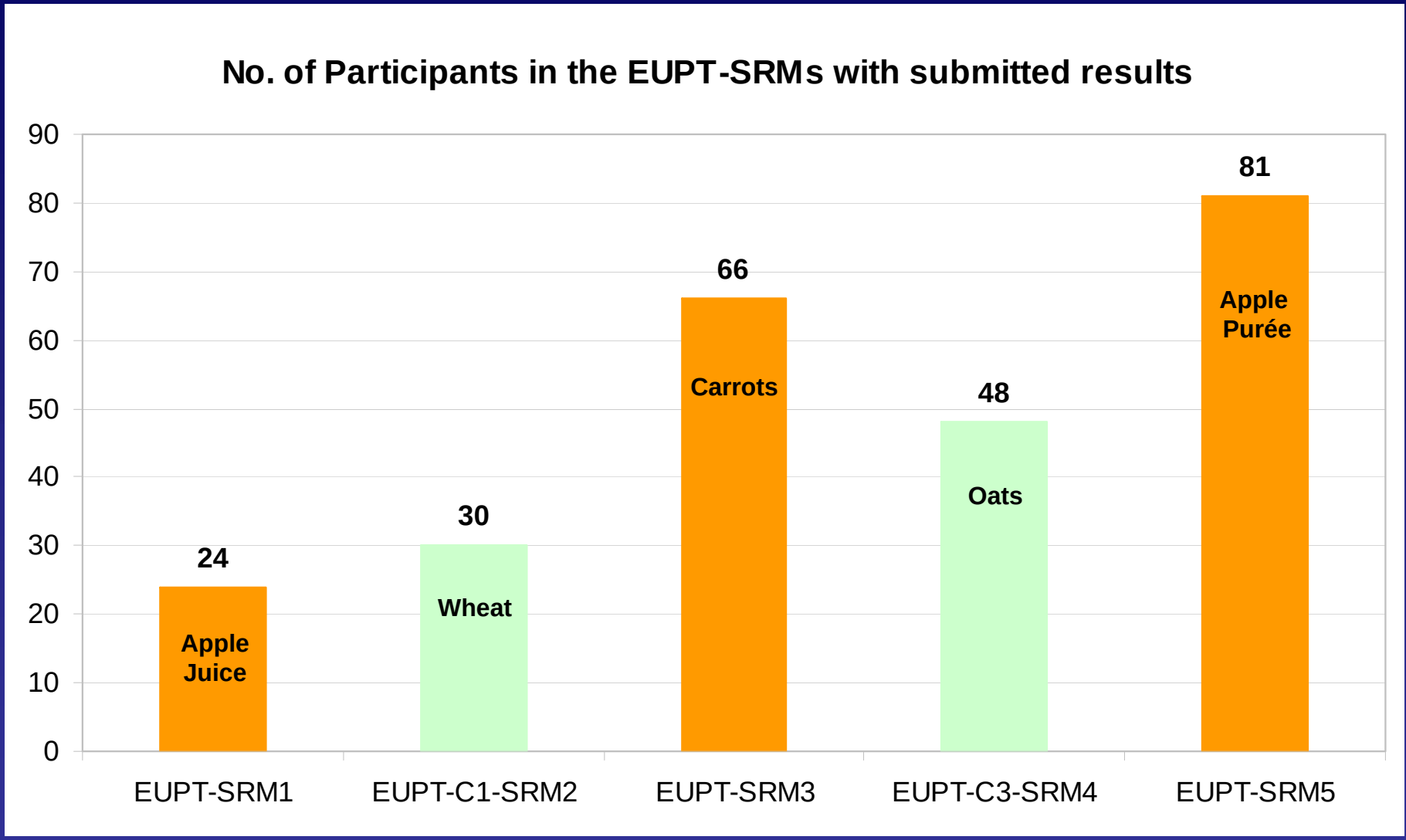
Ethephon:

Dilution and LC-MS/MS	**EURL-Approach**	**52%**
	Other	**10%**
Derivatization + GC:		**7%**
Cleavage to ethylene + GC		**17%**
Using Isotop. labelled ISTD		YES: 28%

EUPT-SRM 1-5

OVERALL EVALUATION

EUPT-SRM 1-5 - OVERALL EVALUATION



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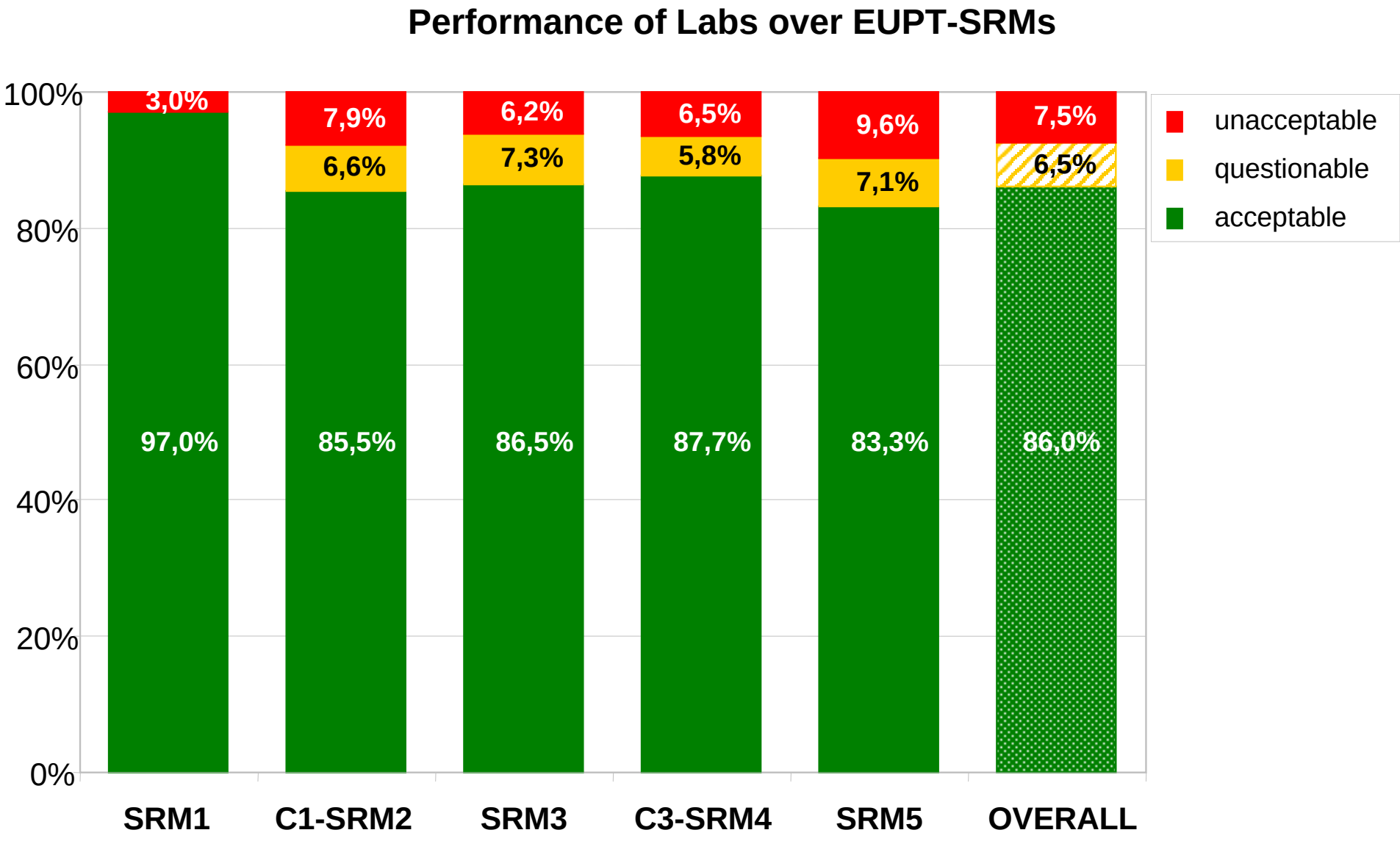

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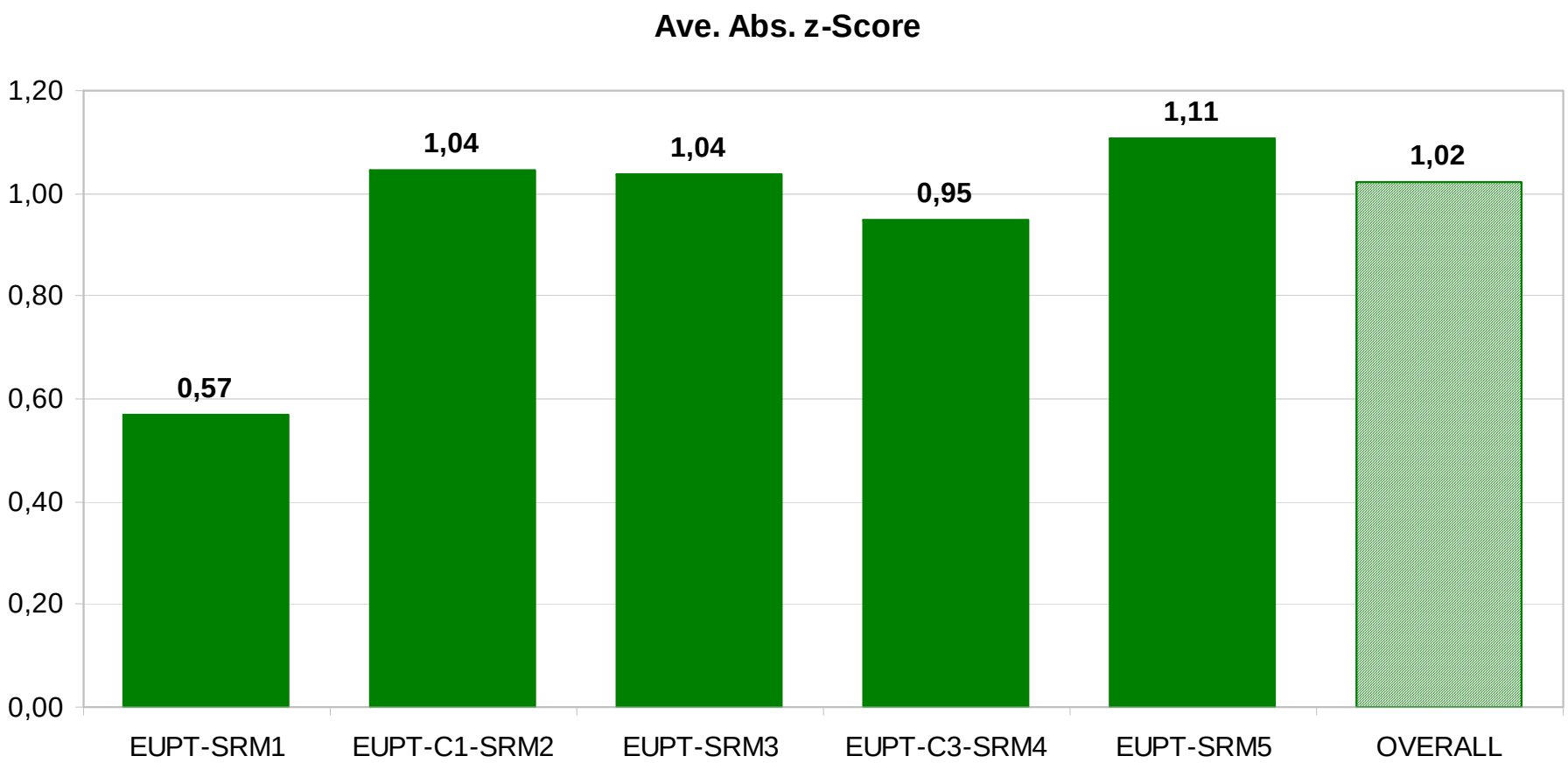
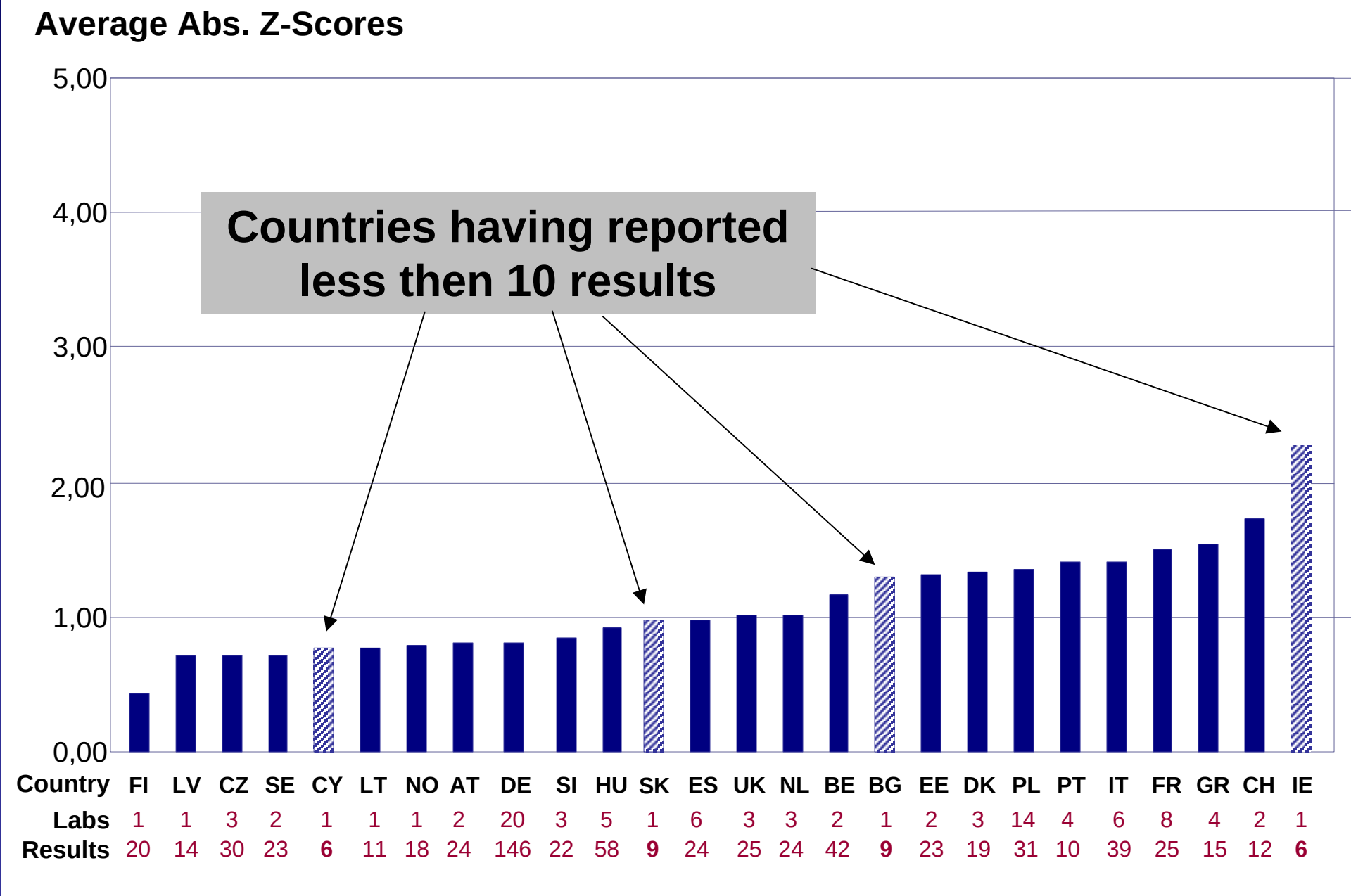
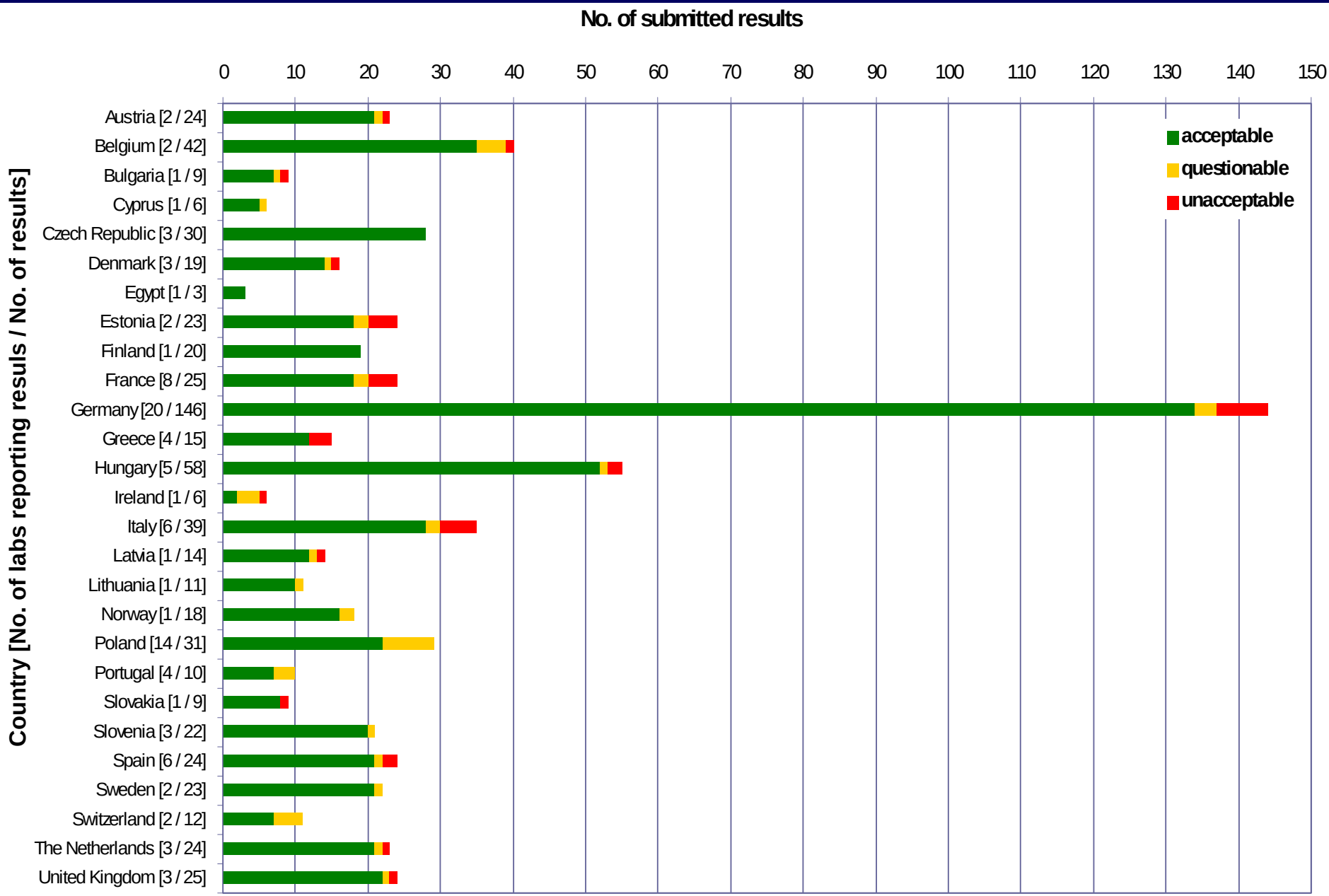


EUPT-SRM 1-5 - OVERALL EVALUATION



Country	FI	LV	CZ	SE	CY	LT	NO	AT	DE	SI	HU	SK	ES	UK	NL	BE	BG	EE	DK	PL	PT	IT	FR	GR	CH	IE
Labs	1	1	3	2	1	1	1	2	20	3	5	1	6	3	3	2	1	2	3	14	4	6	8	4	2	1
Results	20	14	30	23	**6**	11	18	24	146	22	58	**9**	24	25	24	42	**9**	23	19	31	10	39	25	15	12	**6**

EUPT-SRM 1-5 - OVERALL EVALUATION



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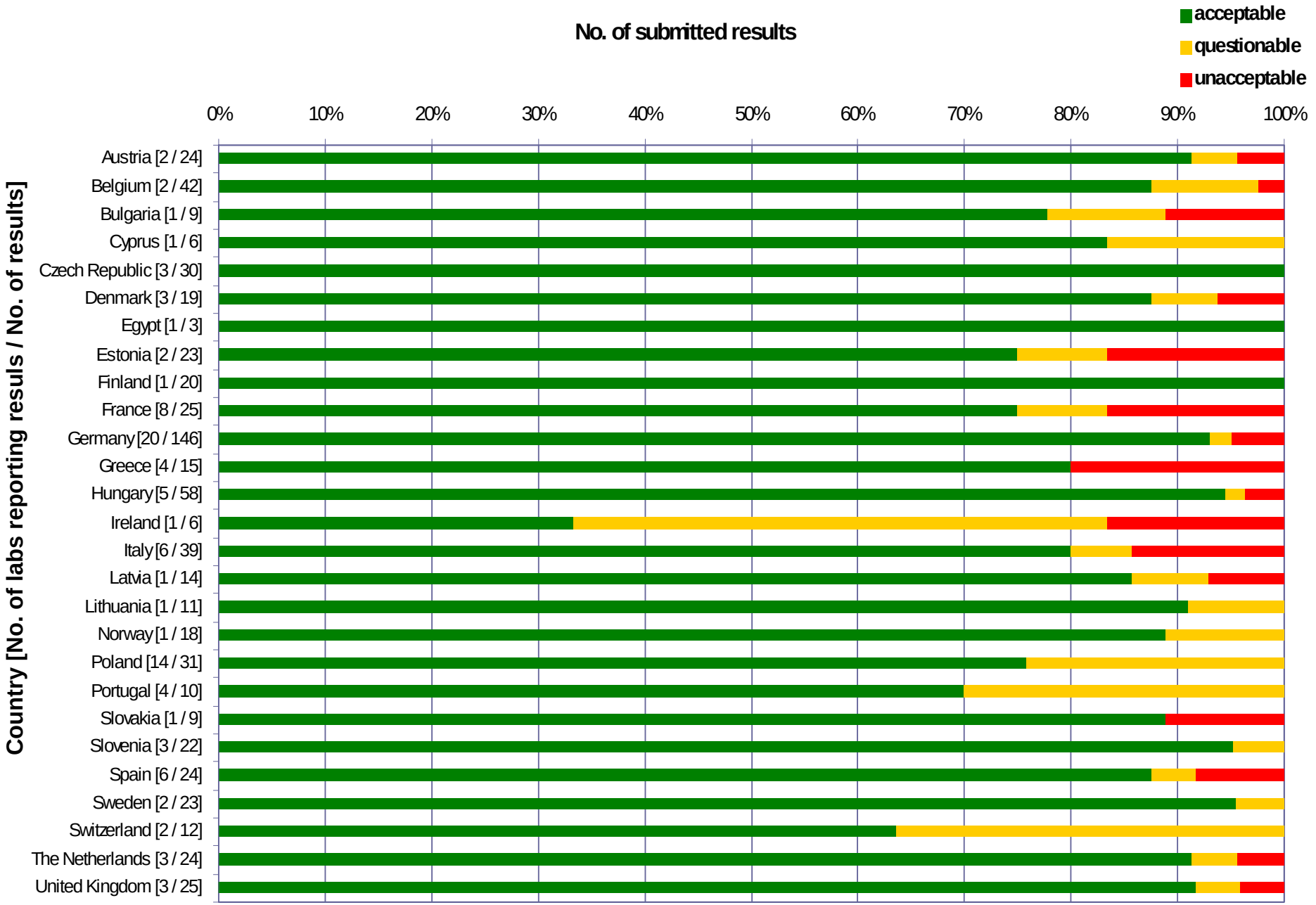


Nicotine in Mushrooms

Nicotine in Mushrooms - Background Information:

- In 2008 high levels of Nicotine detected in mushrooms at CVUA Sigmaringen
- CVUA Stuttgart consulted for confirmation (LC-TOF, -MS/MS ✓ GC-MS ✓)
- Since then many findings by various labs in mushrooms mainly from China
- Most affected dried Porcini (Boletus edulis) but also Truffles and Chanterelles
- Boletus are reported to be not cultivable
- China (Yunnan Region) largest producer (80% of EU-imports from CN)
- Tobacco also widely cultivated in Yunnan region
- Nicotine is a naturally occurring alkaloid in tobacco (*Nicotiana tabacum*) - concentrations 2 - 8%

- Cross-contamination in drying/packing sites may be an issue
- Intentional use of nicotine as pesticides is also speculated

Source of contamination

not clarified yet,

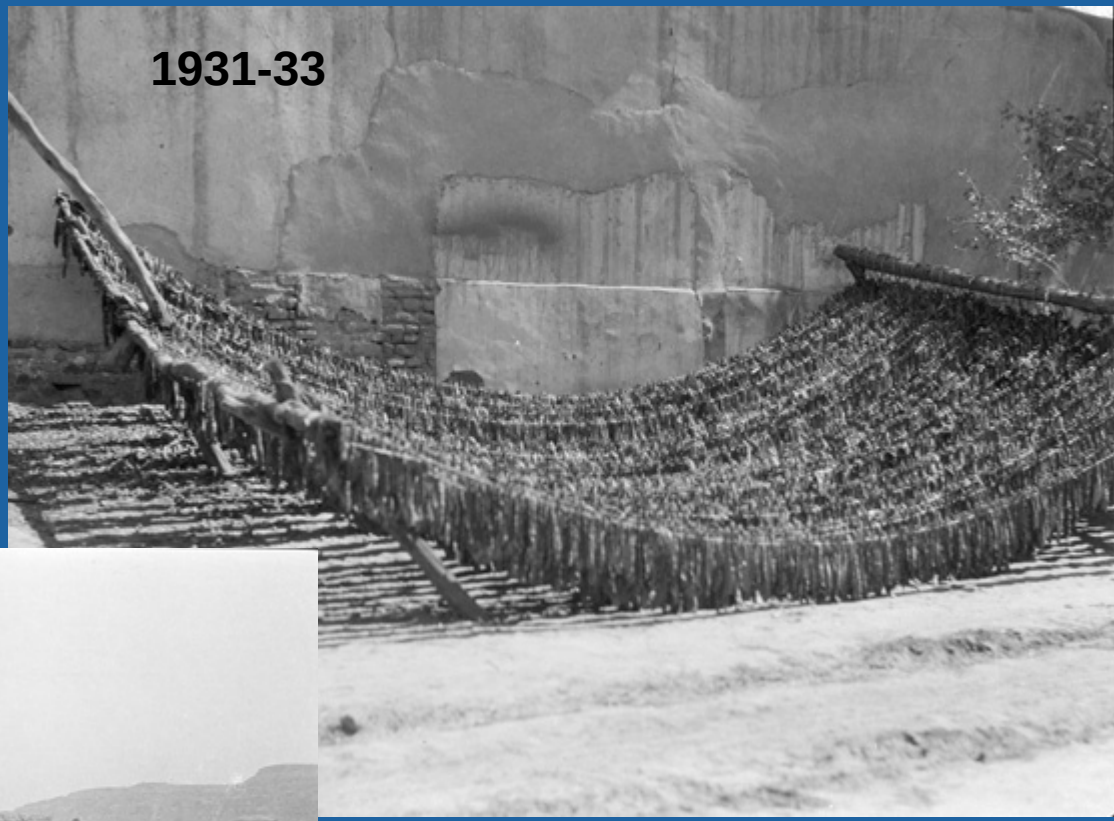
...many possibilities...

- Cross-contamination in drying/packing sites may be an issue
- Intentional use as pesticide in growing areas or during storage
- Natural occurrence in mushrooms
- Natural formation during drying process
- Contamination during harvest via contact with smokers' hands

Other drying practices…

Traditional tobacco drying in China

Source: http://library.duke.edu/digitalcollections



Processing Practices in China

Source: http://www.sinohost.com/yunnan_pages/mushrooms/boletuspreparing.html

Harvest season for fresh boletus: mid May - mid October

Boletus are picked, cleaned, selected and dried
by home-based units run by the farmers
(fresh boletus quickly spoils and must be processed ASAP)

Fresh boletus is dried in open-bottom boards
with many bamboo drawers). Boletus are put fresh
into the drawers and wood fire is lighted beneath.
(are residuals of tobacco plants also disposed this way?)

The drying process for a batch of 200 kg fresh boletus takes
around 6 hours and is controlled by experienced humans.
8-10 kg fresh boletus give ca. 1 kg dried product
with ca. 11% residual water

Post-harvest treatments before exporting are common
a. with fumigants to kill the worms.
b. by ^{60}Co-irradiation to avoid worm breeding.


Drying board


Sorting


Final product

Chinese Commodity Inspection Bureau (CCIB) issues Quality Certificates

Nicotine in Mushrooms – Risk assessm./management

ARfD : 0.0008 mg/kg body weight;
ADI: 0.0008 mg/kg bw per day

EFSA: Data by EU food & drink industries confederation (CIAA) + official labs : 99% of dried mushroom samples contained Nicotine (conc. often above 1 ppm)

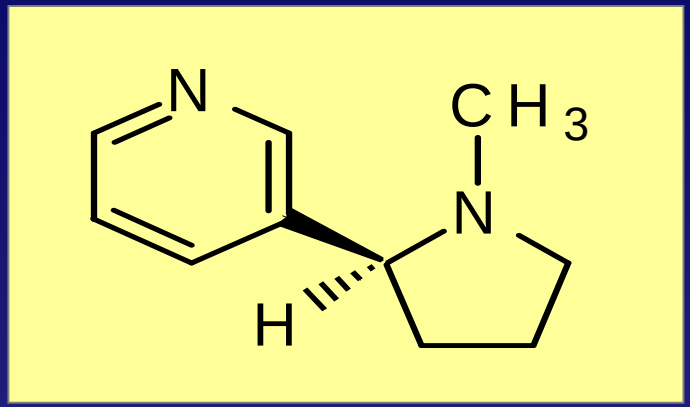
MRLs:

In the past: default MRLs (396/2005/EC) at 0.01mg/kg
In-between: provisional MRLs as proposed by EFSA
Now: Legally binding MRLs

- *Fresh wild mushrooms : 0.04 mg/kg*
- *Dried wild mushrooms other than Ceps (=porcini=boletus): 1.2 mg/kg*
- *Dried Ceps (Boletus): 2.3 mg/kg*

Ad-hoc-Monitoring program for wild mushrooms initiated to help MRL-adjustments in future

NICOTINE PROPERTIES



- **Basic:**

pKa_1 = 3.1; pKa_2 = 8.2
(i.e. predominantly protonated at pH<8.2 and double protonated at pH<3.1)

- **Polar:**

logP = 0.93 (25 °C/unionised) , the lower the pH the lower the logP

- **Volatile:**

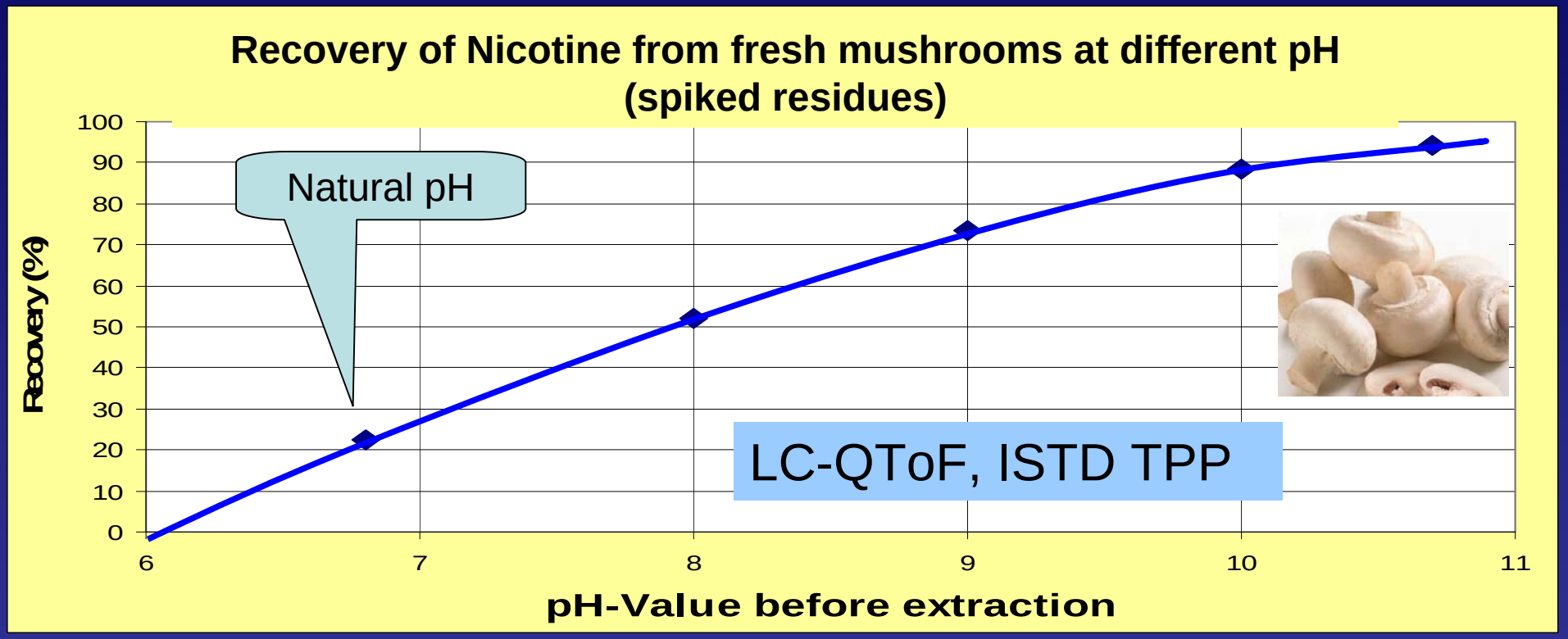
Pvap = 5.6 Pa (25 °C). Evaporation losses reduced at low pH (ionized)

Volatility Comparison:

Biphenyl: 30 Pa (20°C); Dichlorvos: 2.1 Pa (25°C); Methamidophos: 0.0023 Pa (20°C)

(K. Chamberlain et al., Pestic. Sci., 47, 265 (1996)

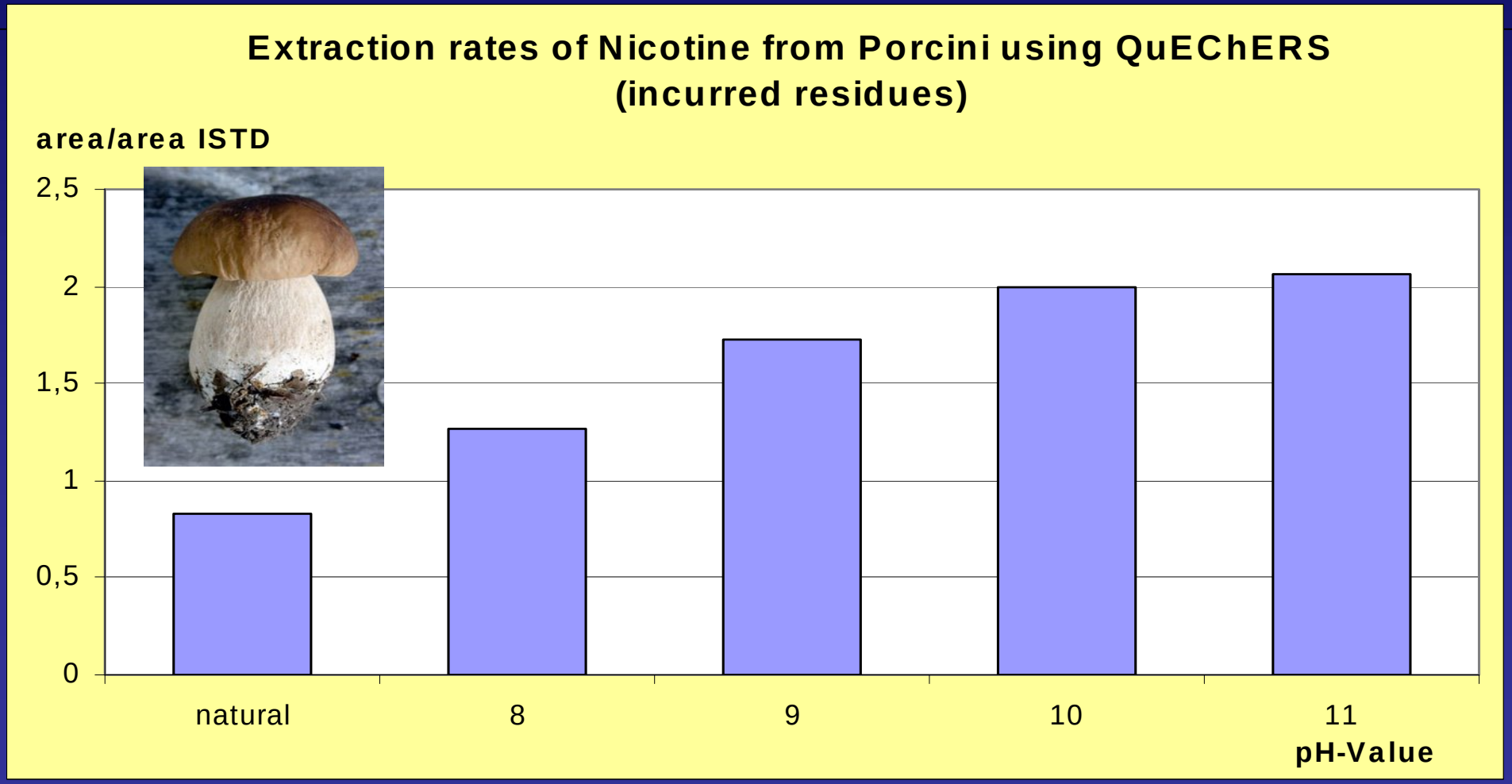
QuEChERS – Optimisation of pH at extraction/partitioning step



Using Nicotine-D3 as ISTD, losses were compensated (rec. 93 - 120 %)
On average 106%

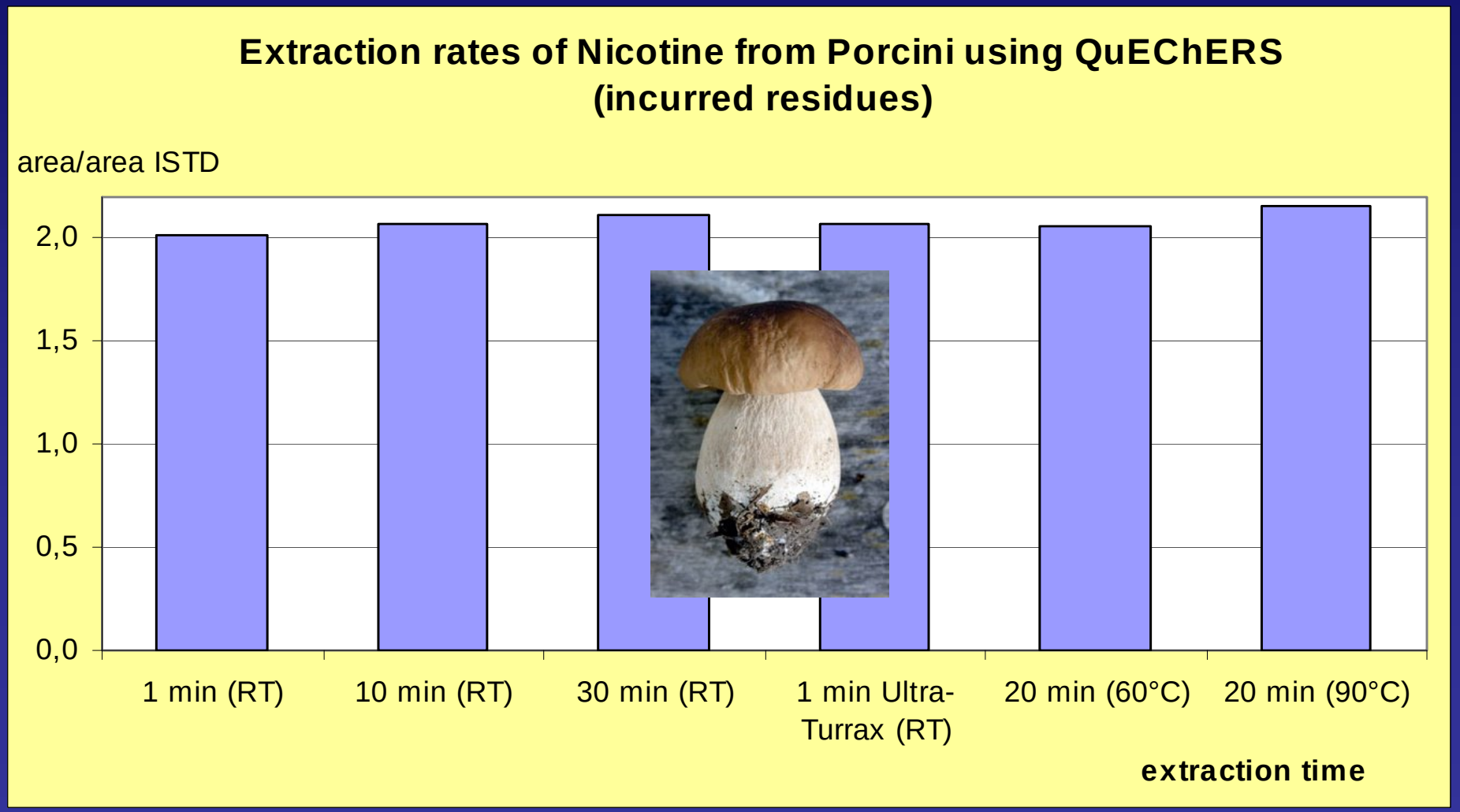
Extraction of **incurred residues** from Dried Porcini

QuEChERS - impact of pH

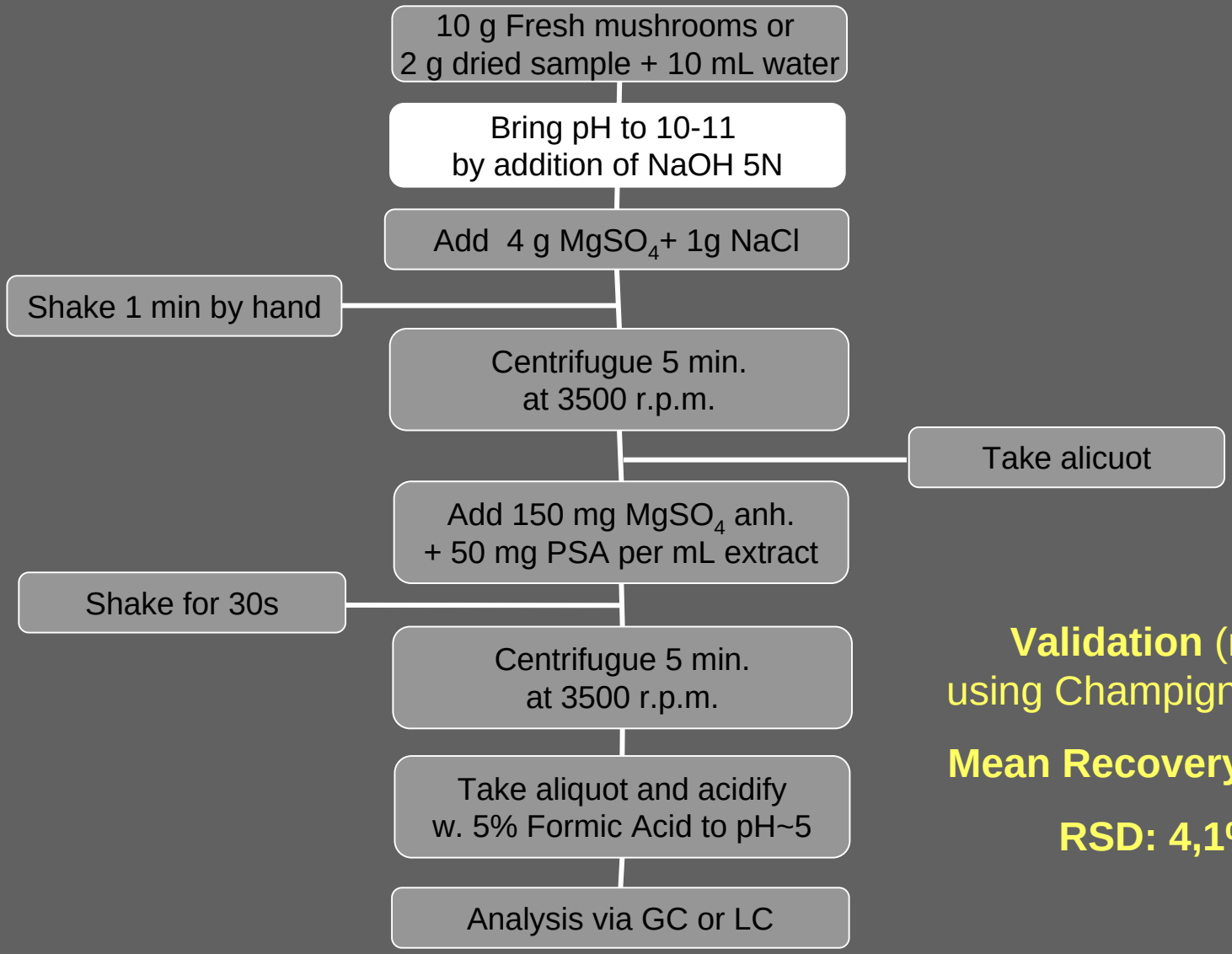


Extraction of **incurred residues** from Dried Porcini

QuEChERS pH 10, Variation of Temperature and Time



QuEChERS modification for Nicotine



Validation (n=5)
using Champignon 10 g

Mean Recovery: 106%

RSD: 4,1%

Ad-hoc Mini-PT on Nicotine in Mushrooms

(in collaboration with COOP CH)

Final report in CIRCA, go to:
http://www.crl-pesticides.eu/docs/public/tmplt_article.asp?LabID=200&CntID=706&Theme_ID=1&Pdf=False&Lang=EN

Ad-hoc PT on Nicotine in Mushrooms

Aims:

- Need to check methodologies in view of the EU-monitoring program on nicotine in mushrooms

-Need to settle the dispute with the Chinese colleagues as regards nicotine analysis

- Possibly draw some conclusions as regards the impact of certain analytical steps

Samples: 3 samples with incurred Nicotine

- **Mu Err** powder - China
- **Boletus** powder - China
- **Boletus** powder - Bosnia and Herzegovina

Only limited amount of material available,

thus only 14 Laboratories could participate

EUPT-SRM5 on Apple Purée September/October 2010

Sector	Country
Government	AT
Government	CH
Government	CH
Government	CN
Government	DE
Government	DE
Government	DE
Government	DE
Government	ES
Government	FR
Industry	CH
Industry	CH
Industry	CN
Industry	DE

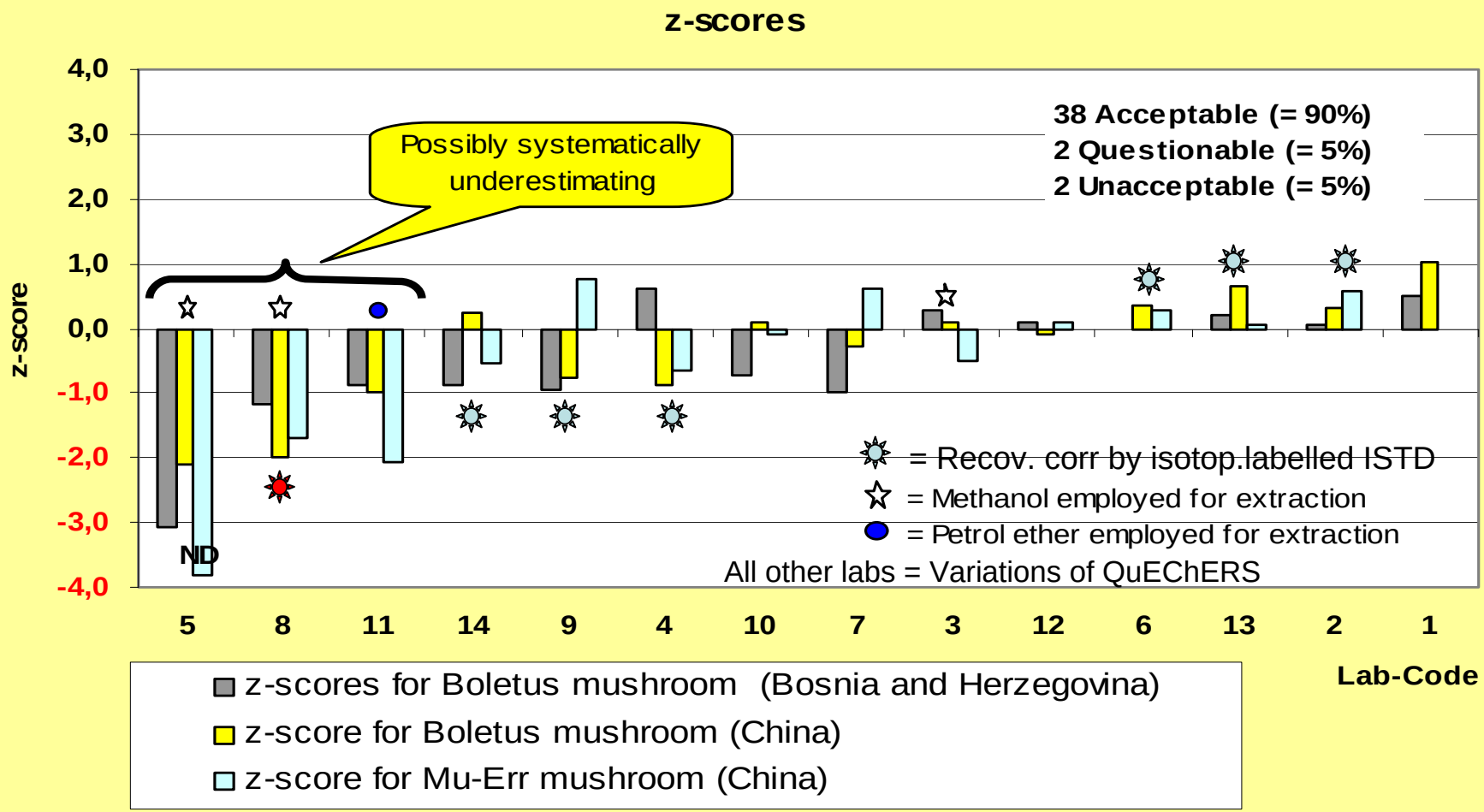
14 laboratories from 6 countries

PT on Nicotine in dried mushrooms- Overall performance

	Boletus BiH	Boletus CN	Mu-Err CN	Overall
Qn-RSD (%)	*23.6*	*29.4*	*23.6*	*26 %*
Median (mg/kg)	*1.01*	*0.72*	*2.56*	
Acceptable	13	13	12	**38 (90%)**
Questionable	0	1	1	**2 (5%)**
Unacceptable	1	0	1 (false neg.)	**2 (5%)**

Acceptable: $|z| \leq 2$,
Questionable $2 < |z| \leq 3$,
Unacceptable $|z| > 3$

PT on Nicotine in dried mushrooms - Z-scores



Final report: http://www.crl-pesticides.eu/library/docs/srm/PT_Nicotine_FinalReport_public.PDF

Other Residue findings in wild mushrooms -
CVUA Stuttgart results in 2009 of 15 dried boletus

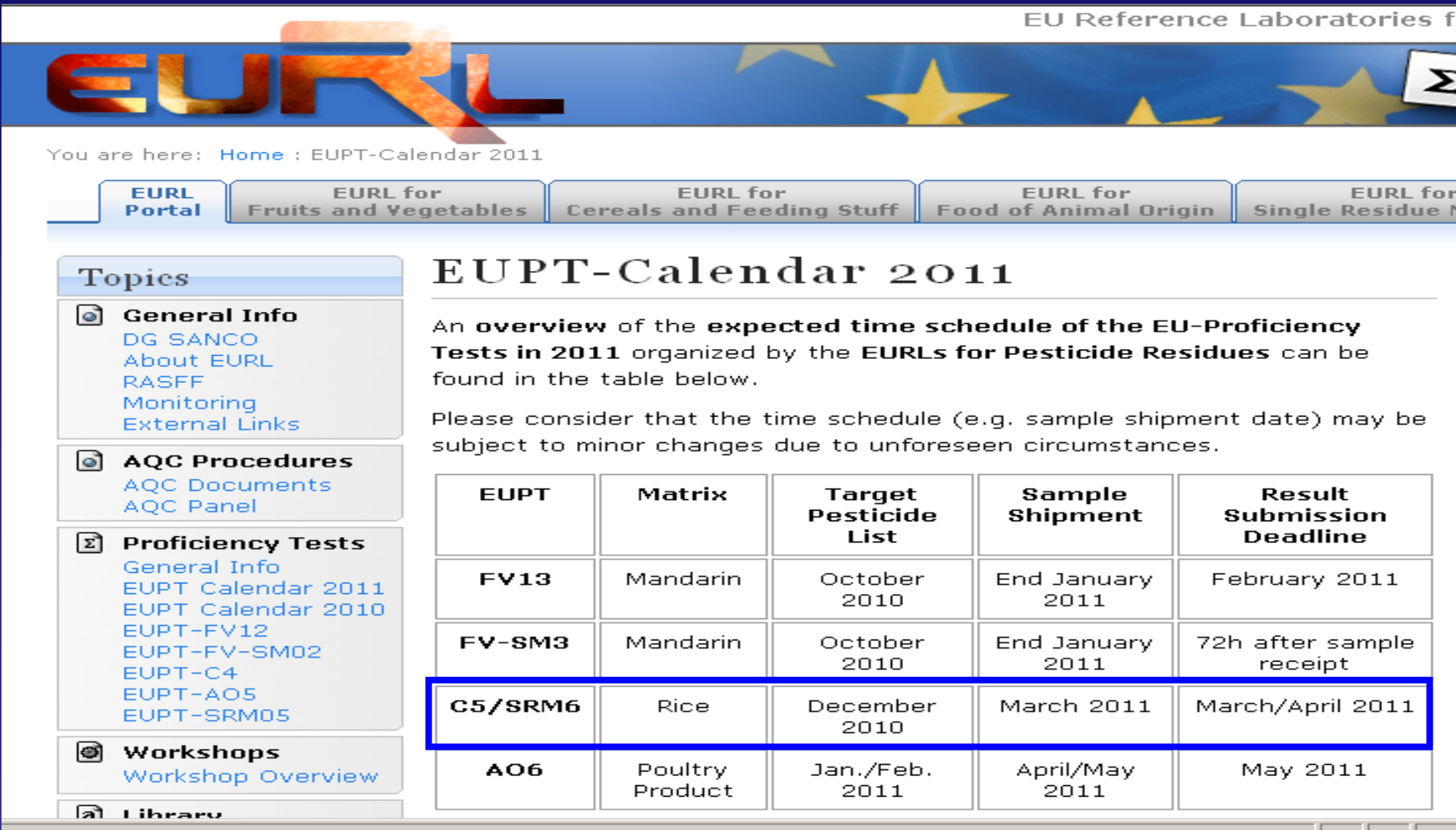
Compound	Detections	Remarks
Nicotine	15 (5 >MRL of 2.3 mg/kg)	**CN: 0,65-4.8 mg/kg; unknown 0.8-8.2 mg/kg; SB: 0.3 mg/kg**
Propoxur	13 (6>MRL)	**All from CN and „unknown“ positive max. 0.31 mg/kg**
Tetramethrin	11 (11>MRL)	**max.: 2 mg/kg; MRL=0.01 mg/kg**
Cypermethrin	13	**max.: 1 mg/kg; MRL= 1 mg/kg**
Permethrin	10 (3>MRL)	**max.: 1.4 mg/kg; MRL=0.05 mg/kg**
Prometryn	2	**2x Traces <0.01 mg/kg**
Piperonylbutoxide	10	**max.: 1.4 mg/kg; no MRL**
Triazophos	1	**Traces <0.01 mg/kg**
Fomesafen	1 (1>MRL)	**0.11 mg/kg ; MRL=0.01 mg/kg**
Clomazone	1 (1>MRL)	**0.1 mg/kg ; MRL=0.01 mg/kg**
Carbendazim	2	**max.: 0.055 mg/kg; MRL=0.1 mg/kg**
Quizalofop	1	**0.015; MRL=0.05 mg/kg**

Note: the MRLs apply to fresh products. A processing factor of ~9 from fresh to dried mushrooms is to be considered, however not for pesticides used for stock preservation of dried mushrooms (e.g. pyrethroids and carbamates are typical).

EUPT-SRM5 on Apple Purée September/October 2010

Whats next?

EUPT-Calendar 2011



EUPT-Calendar 2011

An **overview** of the **expected time schedule of the EU-Proficiency Tests in 2011** organized by the **EURLs for Pesticide Residues** can be found in the table below.

Please consider that the time schedule (e.g. sample shipment date) may be subject to minor changes due to unforeseen circumstances.

EUPT	Matrix	Target Pesticide List	Sample Shipment	Result Submission Deadline
FV13	Mandarin	October 2010	End January 2011	February 2011
FV-SM3	Mandarin	October 2010	End January 2011	72h after sample receipt
C5/SRM6	Rice	December 2010	March 2011	March/April 2011
AO6	Poultry Product	Jan./Feb. 2011	April/May 2011	May 2011

Whats next?

Update of General Protocol

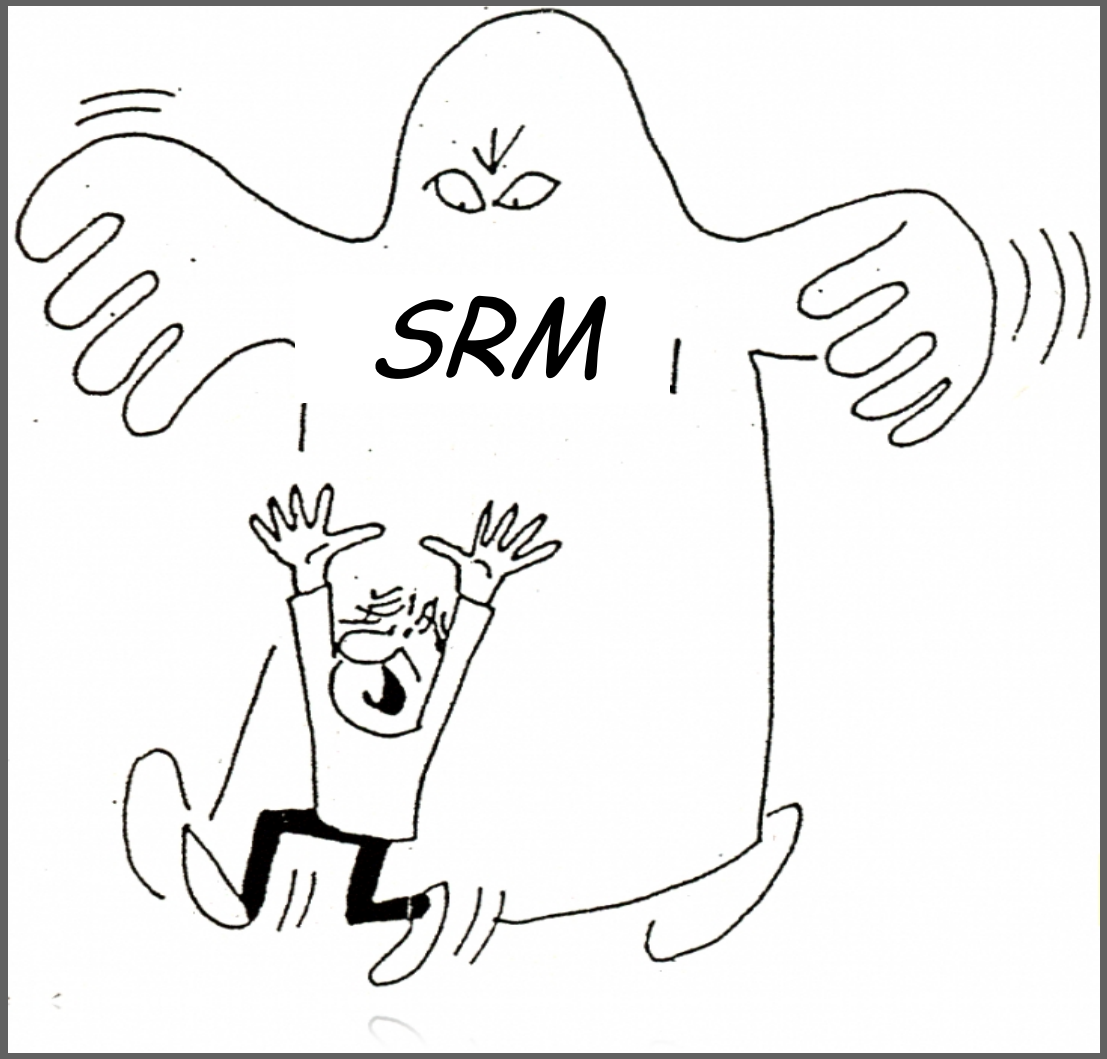
- EURLs will be providing NRLs with codes/results of OFLs within their network
  Why?: NRLs responsible for evaluating + improving the performance of OfL within their network
- EURLs will be also exchanging the EUPT-data among themselves for the purpose of overall performance evaluations

(DG SANCO is owner of all EUPT data)

- Joint Web-based EUPT-database (for all EURLs) is under construction. Will allow …

  a) OfLs to access and evaluate own data

  b) NRLs to access and evaluate data of labs within their network



Thank you very much
for your attention!