



EUPT AO 16

Preparation of Test Material Homogeneity and Stability Tests Evaluation of the Results

Joint Workshop in Almeria and online, 20-22 October 2021



EURL-AO



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Time schedule EUPT AO 16

Actor	Activity	Date
EURL	Preliminary Announcement matrix liquid whole egg at EURL-NRL workshop	1.October 2020
EURL	First Information supplied to laboratories and call for participation	Mid of January 2021
Participant	Registration via EUPT website (new preliminary dates!)	15 February 2021; ending 05 March 2021
Participant	Proof of data entered into the EUPT webtool	By 16 April 2021
Participant	Entering of the analytical scope	Ending 16 April 2021
EURL	Shipment of test material	19 April 2021
Participant	Confirmation of test material receipt	Within 7 days
Participant	Reporting of test results and method information	By 21 May 2021*
Participant	Reporting of additional method information (no changes of reported results possible)	Within 7 working days after end of result reporting
EURL	Dispatch of a preliminary report to all participants	By 31 July 2021
EURL	Dispatch of the final report as pdf-file	Approx. end of 2021

on 28th January 2021

since 22th March 2021

on 9th July 2021

*) Please make sure to report your results on time as there will be no extension of the deadline.

Please check the time table on the webpage regularly as minor changes in the time schedule might be possible!

Participants

- 105 registered labs:
 - 1 Lab: The lab has submitted partial results due to COVID-19.
 - 1 Lab: No results submitted; equipment has suffer damages
- 29 different countries

Country	No Labs	Country	No Labs	Country	No Labs
Austria	2	France	11 (+6)	Poland	9 (+1)
Belgium	4 (+1)	Germany	16 (-8)	Portugal	2
Bulgaria	1 (+1)	Greece	3 (+1)	Romania	2
Croatia	2 (-3)	Hungary	4	Slovakia	3 (+2)
Cyprus	1	Ireland	1	Slovenia	1
Czech Republic	3 (-1)	Italy	13 (-4)	Spain	9 (-10)
Denmark	2 (+1)	Latvia	1	Sweden	2
Estonia	1 (-2)	Lithuania	1	United Kingdom	2 (+1)
Finland	1 (-1)	The Netherlands	4	Iceland	0 (-1)
Norway	1 (-1)	Switzerland	1	North Macedonia	1 (+1)
European Union	25	EFTA	2	3rd Countries	1
Candidate countries	1	Northern Ireland: The Netherlands (NRL), United Kingdom (OFL) Luxembourg: Belgium (NRL), Malta: not confirmed			

→ 102 EU/EFTA Labs

Target list of 102 pesticides

- 61 analytes are mandatory
 - 12 pesticides spiked into the test item
- 41 analytes are voluntary (13 new)
 - 4 voluntary spiked into the test item

NEW: Excel list in CIRCA-BC platform

Version 28 01 2021

EURL EUROPEAN UNION REFERENCE LABORATORY

PESTICIDES RESIDUES IN FOOD OF ANIMAL ORIGIN & COMPOSTS WITH HIGH FAT CONTENT

EURL AO Pesticide Target List for EUPT AO 16
 Liquid Whole Egg Test Item
 List of analytes and MRRL values (all analytes mg/kg product)
 Results shall be rounded to three significant figures (e.g. 0.0581, 0.251 or 1.35).

Legend
 * Results for Spinosad should be reported either if individual standards for Spinosyn A and D or a mixture of Spinosyn A and D are used for calibration.
 ** Results for Spinosyn A or D should be reported, if the individual standards were used for quantification
 New in list of voluntary pesticides

Target List of Mandatory Analytes (Annex 1)

Analyte	Name EURL Datapool	CAS number	Mandatory	Voluntary	EFSA Code	MRRL (mg/kg)
4,4'-Methoxychlor	Methoxychlor	72-43-5	yes	no	RF-0295-001-PPP	0.01
Aldrin	Aldrin	309-00-2	yes	no	RF-0021-002-PPP	0.01
alpha-Endosulfan	Endosulfan, alpha-	959-98-9	yes	no	RF-0155-004-PPP	0.01
alpha-HCH	HCH, alpha-	319-84-6	yes	no	RF-0238-001-PPP	0.01
Azinphos-ethyl	Azinphos-ethyl	2842-71-9	yes	no	RF-0032-001-PPP	0.01
Azinphos-methyl	Azinphos-methyl	86-50-0	yes	no	RF-0033-001-PPP	0.01

Target list of mandatory pesticides

Analyte	MRRL [mg/kg]	Analyte	MRRL [mg/kg]	Analyte	MRRL [mg/kg]
1 Aldrin	0.01	21 Endosulfan alpha	0.01	41 Indoxacarb (sum of isomers)	0.01
2 Azinphos-ethyl	0.01	22 Endosulfan beta	0.01	42 Lambda-cyhalothrin (sum of isomers)	0.01
3 Azinphos-methyl	0.01	23 Endosulfan sulfate	0.01	43 Lindane	0.01
4 Bifenthrin	0.01	24 Endrin	0.005	44 Malathion	0.01
5 Chlordane-cis	0.005	25 Famoxadone	0.01	45 Methidathion	0.01
6 Chlordane-oxy	0.005	26 Fenthion	0.01	46 Methoxychlor	0.01
7 Chlordane-trans	0.005	27 Fenthion oxon	0.01	47 Nitrofen	0.01
8 Chlorfenvinphos	0.01	28 Fenthion oxon sulfone	0.01	48 Parathion-ethyl	0.01
9 Chlorobenzilate	0.01	29 Fenthion oxon sulfoxide	0.01	49 Parathion-methyl	0.01
10 Chlorpyrifos	0.01	30 Fenthion sulfone	0.01	50 Pendimethalin	0.01
11 Chlorpyrifos-methyl	0.01	31 Fenthion sulfoxide	0.01	51 Permethrin (sum of isomers)	0.01
		Fenvalerate and Esfenvalerate (Sum of RR/SS and RS/SR isomers)	0.01	52 Phosmet	0.01
12 Cyfluthrin (sum of isomers)	0.01	32 isomers)	0.01	53 Phoxim	0.01
13 Cypermethrin (sum of isomers)	0.01	33 Fipronil	0.005	54 Pirimiphos-methyl	0.01
14 DDD-pp	0.01	34 Fipronil-Sulfone	0.005	55 Profenofos	0.01
15 DDE-pp	0.01	35 HCH-alpha	0.01	56 Pyrazophos	0.01
16 DDT-op	0.01	36 HCH-beta	0.01	57 Quintozene	0.01
17 DDT-pp	0.01	37 Heptachlor	0.01	58 Resmethrin (sum of isomers)	0.01
18 Deltamethrin (cis-deltamethrin)	0.01	38 Heptachlorepoxyd-cis-	0.01	59 Tecnazene	0.01
19 Diazinon	0.01	39 Heptachlorepoxyd-trans	0.01	60 Triazophos	0.01
20 Dieldrin	0.01	40 Hexachlorobenzene	0.01	61 Vinclozolin	0.01

Spiked analytes (16 analytes)

Target list of voluntary pesticides

Analyte	MRRL [mg/kg]	Analyte	MRRL [mg/kg]	Analyte	MRRL [mg/kg]
1 Benzovindiflupyr	0.01	21 Molinate	0.01	41 Thiophanate-methyl	0.01
2 Bixafen	0.01	22 Oxadiargyl	0.01		
3 Boscalid	0.01	23 Oxasulfuron	0.01		
4 BTS 44595 (prochloraz metabolite)	0.01	24 Oxyfluorfen	0.01		
5 BTS 44596 (prochloraz metabolite)	0.01	25 Penflufen	0.01		
6 Carbendazim	0.01	26 Penthiopyrad	0.01		
7 Chlorpropham	0.01	27 Picolinafen	0.01		
8 Cyproconazole	0.01	28 Prochloraz	0.01		
9 Epoxiconazole	0.01	29 Propaquizafop	0.01		
10 Etofenprox	0.01	30 Prothioconazole-desthio	0.01		
11 Fenpropidin	0.01	31 Quinoclamine	0.01		
		Spinosad (sum of spinosyn A and			
12 Fenpropimorph	0.01	32 spinosyn D, expr. as spinosad)*	0.01		
13 Fenpyrazamine	0.01	33 Spinosyn A**	0.01		
14 Fluopyram	0.01	34 Spinosyn D**	0.01		
15 Fluquinconazole	0.01	35 Spiroxamine	0.01		
16 Flusilazole	0.01	36 Sulfoxaflor	0.01		
17 Hydroxy-Tebuconazole	0.01	37 Tau-Fluvalinate	0.01		
18 Mefentrifluconazole	0.01	38 Tebuconazole	0.01		
19 Metaflumizone	0.01	39 Tetraconazole	0.01		
20 Metconazole (sum of isomers)	0.01	40 Thiocloprid	0.01		

* Results for Spinosad should be reported either if individual standards for Spinosyn A and D or a mixture of Spinosyn A and D are used for calibration.

** Results for Spinosyn A or D should only be reported, if the individual standards were used for quantification!

Voluntary analytes (41 analytes)

Spiked analytes (16 analytes)

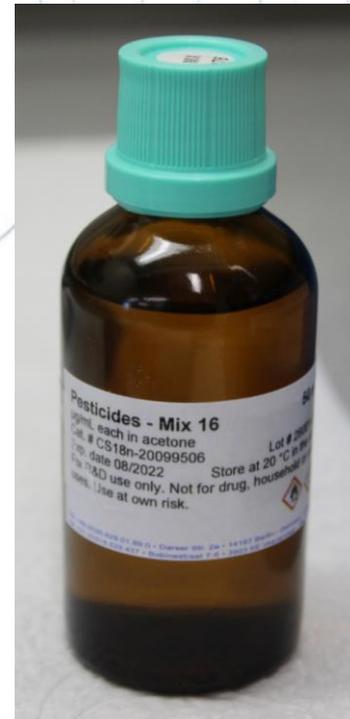
New in list of voluntary pesticides

→ from Working Document SANCO/12745/2013 and to cover full residue definition

Preparation

- 10 kg of liquid whole egg from a local wholesaler
 - tested to be “free” of relevant pesticide residues

- 1 Certified spiking solution
 - custom made by CAMPRO Scientific GmbH
 - solvent: acetone
 - checked against EURL-standards



Preparation

- Spiking of 20.0 ml of the certified spiking solution in 10 kg of liquid whole egg
- Homogenisation by stirring for 2h
- Bottling min. 50 g in test items (no blank material provided)



Mandatory pesticides			
Cyfluthrin	DDE-pp	Deltamethrin	Diazinon
Endrin	Fipronil-sulfone	Lambda-cyhalothrin (sum of isomers)	Lindane
Parathion-ethyl	Phoxim	Pyrazophos	Quintozene
Voluntary pesticides			
Bixafen	Hydroxy-Tebuconazole	Tau-Fluvalinate	Thiacloprid



EUROPEAN UNION REFERENCE LABORATORY

PESTICIDES RESIDUES IN FOOD OF ANIMAL ORIGIN & COMPARABLE MEDIA WITH HIGH FAT CONTENT

Methods

Analysis of GC amenable pesticides with modified QuEChERS (EN 15662) method (Q-EMR method) in egg

Start:

- Weigh 5.0 g \pm 0.1 g of liquid whole egg into a 50 mL centrifuge tube
- Add internal standard solution, vortex or shake for a few seconds and wait for at least 10 min

Extraction procedure:

- Add 10 mL water and 200 μ l methanol for a sample weight of 5 g
- Add 10 mL acetonitrile
- Shake for 10 min (shaker)
- Add extraction salts (3 g sodium chloride, 1 g trisodium citrate x 2 H₂O, 0.5 g disodium citrate x 6 H₂O)
- Shake for 10 min (shaker)
- Centrifuge at 2500 g for 5 min
- Add 4 mL water into a 15 mL EMR lipid dSPE centrifugation tube
- Transfer an aliquot of ~4 mL acetonitril-extract in the prepared 15 mL EMR lipid dSPE centrifugation tube
- Shake for 10 min (shaker)
- Centrifuge at 2500 g for 5 min
- Transfer the whole supernatant into a 15 mL EMR lipid Polish centrifugation tube (with 500 mg additional magnesium sulfate)
- Shake the tube vigorously for 10 min (shaker) (the tube will become warm)
- Centrifuge at 2500 g for 5 min.
- Transfer an aliquot of the extract into a vial
- Add analyte protections (3 μ l to 100 μ l extract) and employ for GC-MS/MS analysis



EUROPEAN UNION REFERENCE LABORATORY

PESTICIDES RESIDUES IN FOOD OF ANIMAL ORIGIN & COMPARABLE MEDIA WITH HIGH FAT CONTENT

Analysis of Pesticides with modified QuEChERS (EN 15662) method liquid whole egg

Start:

- Weigh 5 g of liquid whole egg into a 50 mL centrifuge tube
- Add internal standard solution (e.g. Carbenidazim-D3), vortex for a few seconds and wait for at least 10-20 min

Extraction procedure:

- Add 10 mL water
- Shake for 10 min (shaker)
- Add 10 mL acetonitrile
- Shake for 10 min (shaker)
- Add extraction salts (4 g MgSO₄, 1 g NaCl, 1 g Na₃-citrate dihydrate and 0.5 g Na₂hydrogen-citrate - sesquihydrate)
- Shake for 10 min (shaker)
- Centrifuge at 2500 g for 5 min
- Transfer an aliquot of the extract into a centrifugation tube which contains 25 mg PSA and 150 mg magnesium sulphate per mL extract. (e.g. for an aliquot of 6 mL: 150 mg PSA and 900 mg magnesium sulphate)
- Shake the tube vigorously for 10 min (shaker) (hint: time can be reduced if necessary)
- Centrifuge at 2500 g for 5 min.
- Transfer an aliquot of the extract into a vial and employ for LC-MS/MS analysis

Homogeneity/Stability test results

Homogeneity test

- 11 randomly selected test portions
(including the first and the last unit portioned)
analysed in duplicate

Stability test

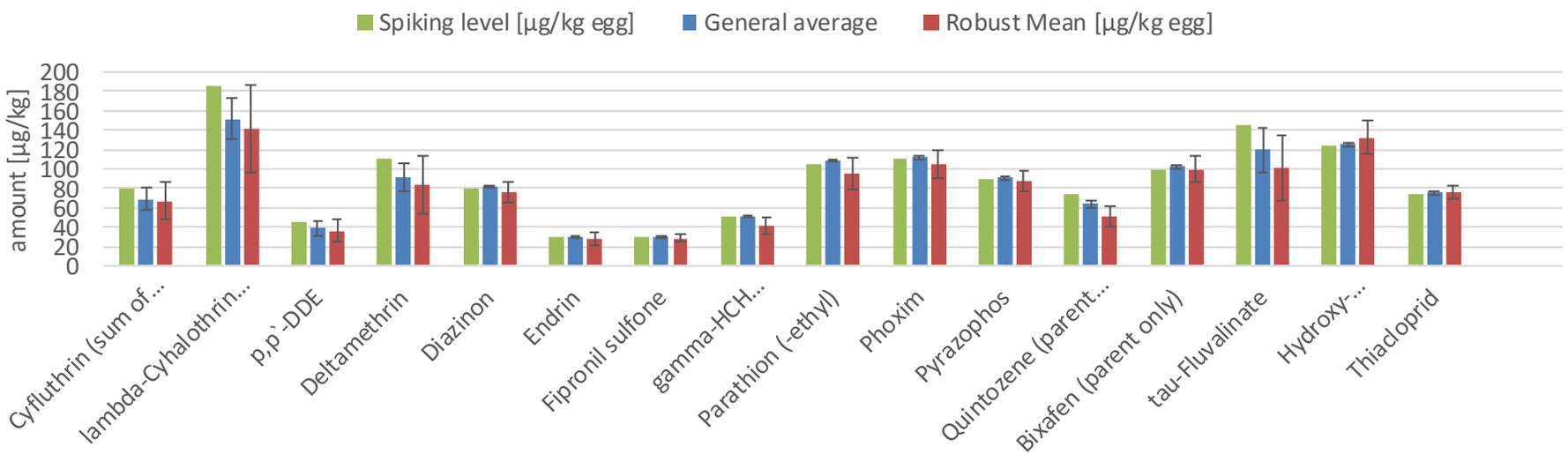
- 3 samples used for homogeneity test were used for stability testing
analysed in duplicate
test I: shipment of test item (20.04)
test II: after deadline of result submission (25.05)
- Statistical evaluation according to
IUPAC/ISO/AOAC International Protocol
for Proficiency Testing **ISO 13528:2020-09**

Homogeneity test results

Sample	Replicate	Cyfluthrin (sum of isomers)	lambda-Cyhalothrin (sum of isomers)	p,p'-DDE	Deltamethrin	Diazinon	Endrin	Fipronil sulfone	gamma-HCH (Lindane)	Parathion (-ethyl)	Phoxim	Pyrazophos	Quintozene (parent only)	Bixafen (parent only)	tau-Fluvalinate	Hydroxy-Tebuconazole	Thiacloprid
1	1	73.8	156.2	47.8	95.8	81.5	29.4	30.6	53.9	107.8	111.4	91.7	71.7	102.4	125.7	125.7	75.4
	2	57.0	126.4	32.0	83.9	81.7	29.9	30.1	50.7	110.4	111.4	88.2	67.7	102.0	99.4	126.6	75.4
46	1	86.0	173.9	48.1	113.7	82.6	30.0	29.9	52.5	108.7	111.9	92.6	68.3	103.7	150.1	125.7	75.0
	2	57.7	132.1	32.2	78.8	82.2	29.6	29.6	51.0	106.6	112.9	90.4	63.9	101.5	101.2	126.1	75.0
138	1	84.8	178.4	47.8	116.8	81.7	29.5	30.1	53.0	107.7	110.6	90.9	70.9	101.7	154.1	124.8	75.3
	2	59.6	136.7	33.2	83.9	81.2	29.7	29.5	51.2	109.4	112.4	91.5	65.7	102.9	104.4	125.3	75.2
23	1	84.7	181.7	48.5	117.9	83.9	29.9	30.5	52.2	110.1	117.7	96.4	68.5	104.3	157.5	133.2	80.2
	2	60.6	146.0	33.7	90.0	81.7	28.6	28.1	50.3	108.1	110.5	90.6	62.2	100.6	111.7	124.9	74.2
111	1	72.6	158.7	44.9	96.0	82.2	30.8	28.9	50.6	108.7	113.0	92.0	67.8	103.6	126.1	124.9	75.4
	2	63.2	148.0	33.2	88.7	81.8	29.9	29.5	50.7	108.0	111.4	89.7	61.9	101.0	115.4	123.9	74.6
142	1	88.2	184.0	51.1	117.9	82.1	30.8	29.9	53.5	106.8	111.2	90.1	66.0	102.3	166.6	124.7	74.9
	2	58.0	129.7	32.8	77.3	82.3	28.8	29.1	51.4	108.1	111.4	90.4	64.9	102.5	101.6	125.6	75.5
133	1	81.5	180.0	43.7	105.7	81.7	30.4	30.2	51.4	106.6	111.3	91.2	62.4	103.6	145.0	124.4	75.5
	2	58.2	134.2	33.7	78.2	80.9	28.1	29.3	50.7	109.2	111.4	89.8	63.5	101.1	100.5	124.7	75.2
175	1	73.1	176.2	42.3	95.7	81.4	30.6	30.1	50.6	108.3	112.4	91.1	60.5	102.5	127.8	125.0	74.8
	2	53.9	125.5	32.0	74.8	82.4	27.6	28.7	50.7	110.4	113.4	92.1	59.9	103.1	99.5	125.9	74.8
87	1	73.1	155.9	43.0	89.2	80.7	30.3	30.8	50.1	106.2	110.6	90.1	61.8	102.3	118.7	124.2	73.4
	2	57.4	129.3	30.5	76.0	80.6	28.6	29.6	50.9	108.0	111.4	90.7	62.9	101.9	94.8	124.3	74.4
63	1	74.8	168.1	42.0	93.0	81.4	31.0	29.8	50.2	109.0	112.8	91.7	57.2	102.1	126.0	125.7	75.6
	2	56.1	123.4	30.6	72.5	80.2	28.9	29.3	49.9	105.6	109.1	88.2	59.8	98.9	89.8	121.9	72.3
195	1	76.1	164.4	47.1	99.6	82.8	30.5	29.5	51.3	110.3	113.2	92.9	64.4	105.6	130.4	126.5	76.3
	2	56.2	132.4	30.0	75.1	80.2	28.2	29.3	50.6	109.0	110.6	89.6	61.7	101.3	93.8	122.9	73.8
General average		68.5	151.9	39.1	91.8	81.7	29.6	29.7	51.2	108.3	111.9	91.0	64.3	102.3	120.0	125.3	75.1
Standard deviation		11.65	21.28	7.44	14.91	0.87	0.97	0.64	1.10	1.39	1.68	1.73	3.75	1.41	22.92	2.09	1.42
Cv		17.0%	14.0%	19.0%	16.2%	1.1%	3.3%	2.1%	2.1%	1.3%	1.5%	1.9%	5.8%	1.4%	19.1%	1.7%	1.9%
Spiking level [µg/kg egg]		80.0	185.0	45.0	110.0	80.0	30.0	30.0	50.0	105.0	110.0	90.0	75.0	100.0	145.0	125.0	75.0
Robust Mean [µg/kg egg]		67.2	141.8	36.1	84.2	76.6	27.9	28.6	41.4	94.9	104.6	87.1	51.5	100.0	101.3	132.4	75.4

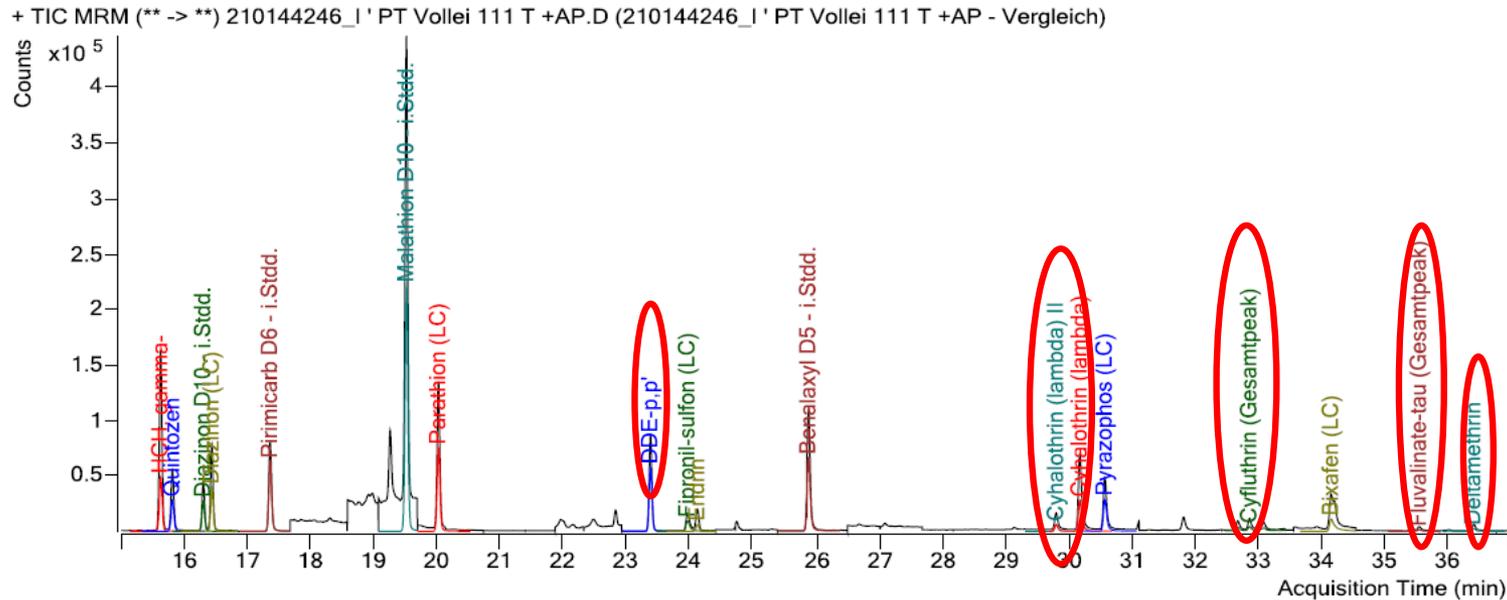
Homogeneity test results

Sample	Replicate	Cyfluthrin (sum of isomers)	lambda-Cyhalothrin (sum of isomers)	p,p`-DDE	Deltamethrin	Diazinon	Endrin	Fipronil sulfone	gamma-HCH (Lindane)	Parathion (-ethyl)	Phoxim	Pyrazophos	Quintozene (parent only)	Bixafen (parent only)	tau-Fluvalinate	Hydroxy-Tebuconazole	Thiacloprid
General average		68.5	151.9	39.1	91.8	81.7	29.6	29.7	51.2	108.3	111.9	91.0	64.3	102.3	120.0	125.3	75.1
Standard deviation		11.65	21.28	7.44	14.91	0.87	0.97	0.64	1.10	1.39	1.68	1.73	3.75	1.41	22.92	2.09	1.42
Cv		17.0%	14.0%	19.0%	16.2%	1.1%	3.3%	2.1%	2.1%	1.3%	1.5%	1.9%	5.8%	1.4%	19.1%	1.7%	1.9%
sw (B.8)		15.50	28.36	9.74	18.32	0.65	1.19	0.76	1.12	1.52	1.93	1.90	2.72	1.49	28.86	2.09	1.57
cv(w)		22.6%	18.7%	24.9%	19.9%	0.8%	4.0%	2.6%	2.2%	1.4%	1.7%	2.1%	4.2%	1.5%	24.0%	1.7%	2.1%
Spiking level [µg/kg egg]		80.0	185.0	45.0	110.0	80.0	30.0	30.0	50.0	105.0	110.0	90.0	75.0	100.0	145.0	125.0	75.0
Robust Mean [µg/kg egg]		67.2	141.8	36.1	84.2	76.6	27.9	28.6	41.4	94.9	104.6	87.1	51.5	100.0	101.3	132.4	75.4
Robust RSD [%]		29.0%	31.7%	31.7%	35.4%	14.0%	23.0%	14.7%	22.2%	16.8%	13.9%	11.8%	21.2%	13.1%	32.9%	12.7%	9.4%

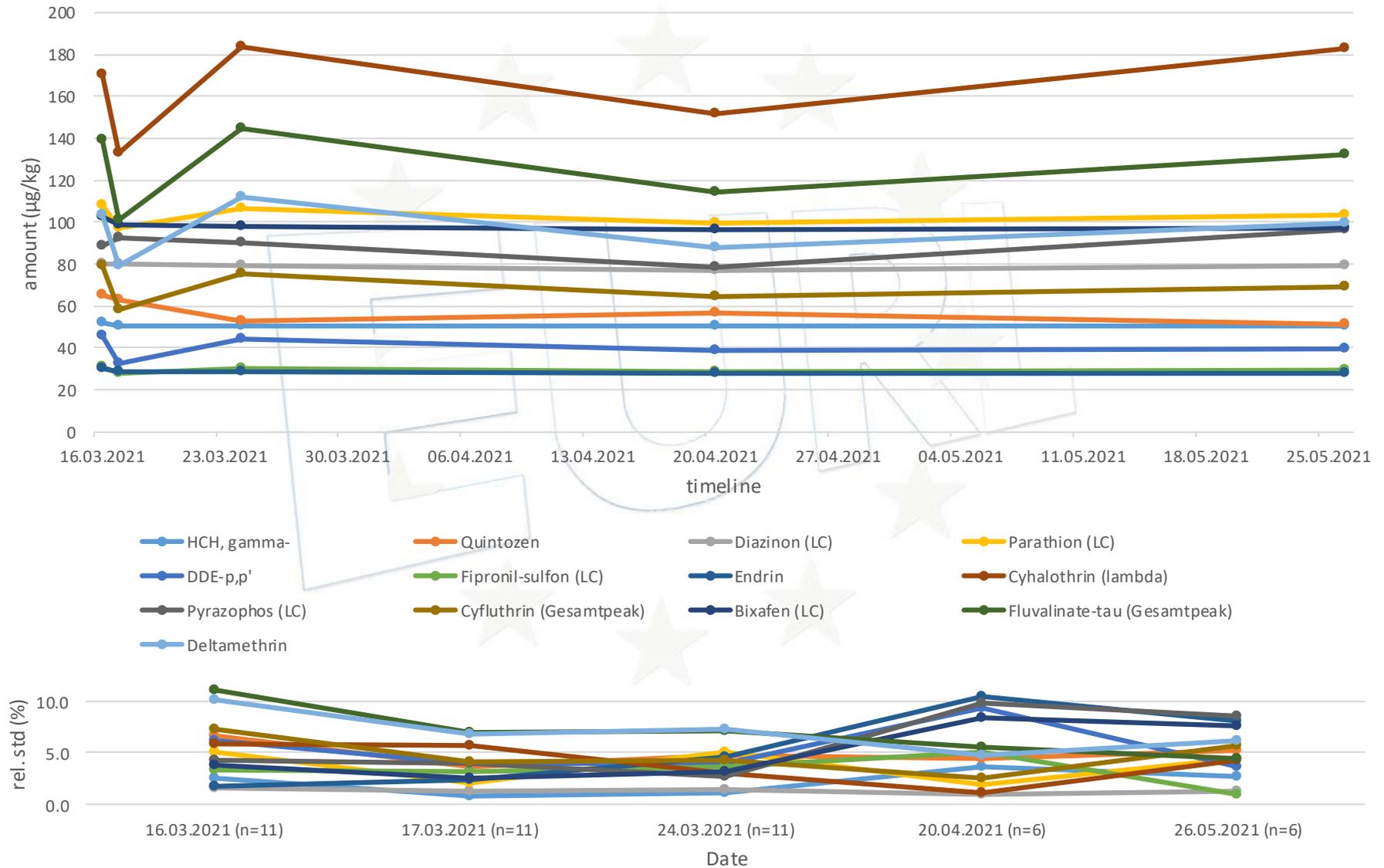


Q-EMR Clean-up: Reason for variance?

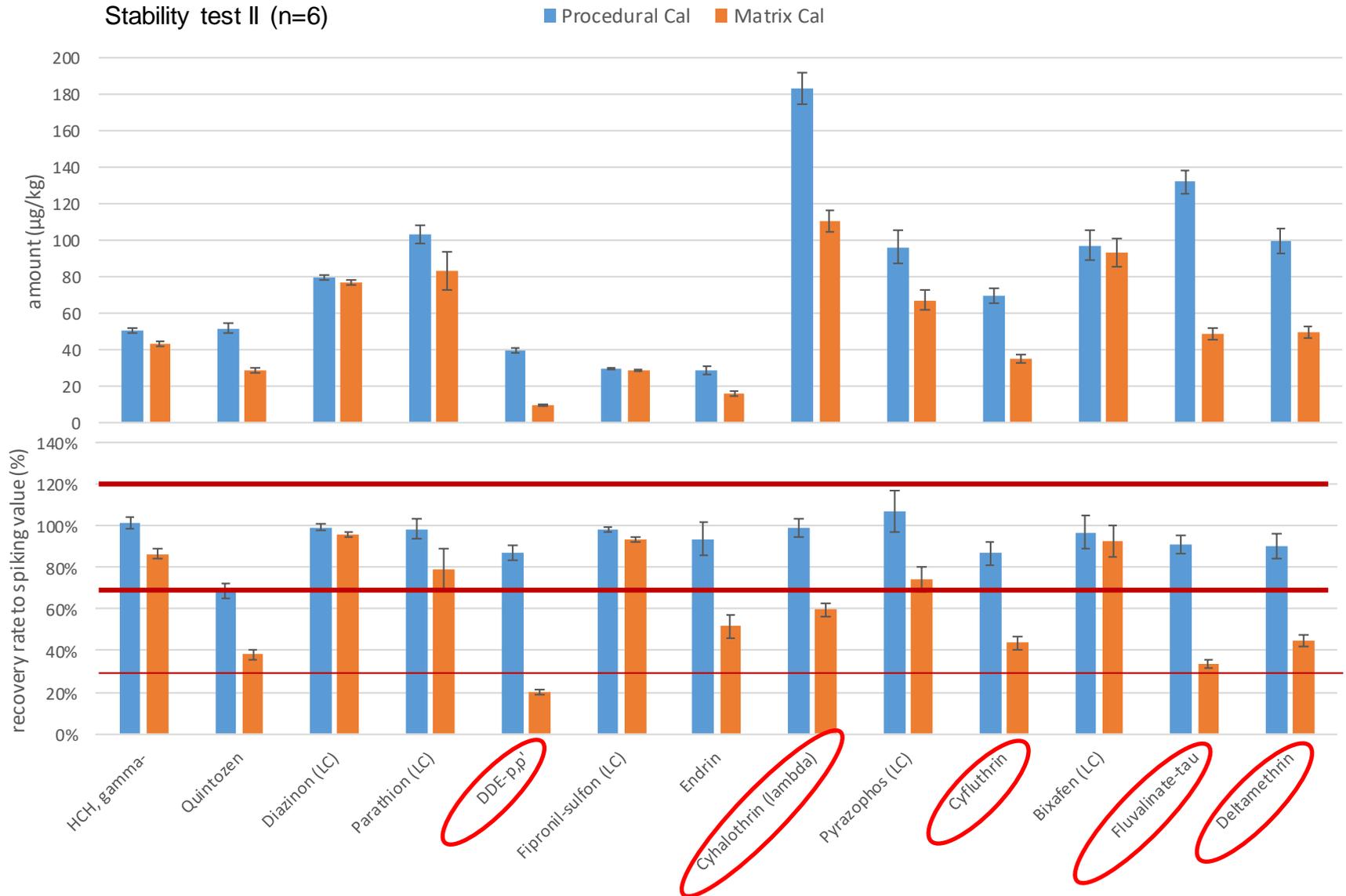
- Repeated sample measurement (homogeneity 1 and 2) in one sequence
 - Determined concentration were confirmed
 - Sample measurement as possible error source excluded
- Internal standards Diazinon D10, Malathion D10 and Benalaxyl D5 show consistent areas in the samples and procedural calibration
- Only some analytes show the variance
 - General sample preparation error excluded



Variation of Q-EMR results



Q-EMR Cleanup: Comparison of Procedural and Matrix Matched Calibration



Stability test results

		Hom test I+II	Stab test I				Stab test II					$ y_1 - y_2 \leq 0.3\sigma$
Date		16.03.2021/ 17.03.2021	20.04.2021		Stab I - Hom	25.05.2021		Stab II - Hom	Stab II - Stab I	ISO 13528:2020-09		
Sample No.		Average	Stabw	%	Average	Recovery	Stabw	%	Average	Recovery	Recovery	Recovery to Hom
mandatory	Cyfluthrin (sum of isomers)	68.5	1.8	2.7	64.3	93.9	4.3	6.2	69.4	101.3	107.9	o.k.
	lambda-Cyhalothrin (sum of isomers)	151.9	1.8	1.2	152.0	100.1	8.5	4.6	182.9	120.5	120.3	o.k.
	p,p'-DDE	39.1	4.0	10.3	38.6	98.6	1.5	3.9	39.3	100.4	101.8	o.k.
	Deltamethrin	91.8	4.5	5.1	88.0	95.9	6.7	6.7	99.1	107.9	112.6	o.k.
	Diazinon	81.7	0.7	0.8	81.0	99.1	0.5	0.6	79.2	97.0	97.8	o.k.
	Endrin	29.6	3.2	11.5	27.8	94.0	2.5	8.8	28.1	95.1	101.1	o.k.
	Fipronil sulfone	29.7	0.7	2.4	29.5	99.5	0.7	2.4	29.3	98.8	99.2	o.k.
	gamma-HCH (Lindane)	51.2	2.0	3.9	50.8	99.1	1.5	2.9	50.6	98.7	99.6	o.k.
	Parathion (-ethyl)	108.3	1.5	1.4	108.3	100.0	0.6	0.5	102.7	94.8	94.8	o.k.
	Phoxim	111.9	1.8	1.6	110.4	98.7	1.1	1.1	107.3	95.8	97.1	o.k.
	Pyrazophos	91.0	0.7	0.8	90.2	99.1	0.5	0.6	89.0	97.8	98.6	o.k.
voluntary	Quintozene (parent only)	64.3	2.8	4.9	56.3	87.5	2.9	5.7	51.4	80.0	91.4	o.k.
	Bixafen (parent only)	102.3	0.9	0.8	101.4	99.1	0.7	0.8	98.6	96.3	97.2	o.k.
	tau-Fluvalinate	120.0	6.9	6.1	114.5	95.4	6.3	4.8	131.8	109.8	115.1	o.k.
	Hydroxy-Tebuconazole	125.3	0.5	0.4	125.5	100.1	1.3	1.0	123.4	98.5	98.3	o.k.
	Thiacloprid	75.1	0.8	1.0	75.3	100.3	0.7	1.0	75.2	100.1	99.8	o.k.

→ All analytes of the proficiency test items are considered to be adequately stable for result submission period.



Results

Statistical Parameters

Evaluation according to general protocol (9th Edition):

- Assigned value:
robust mean
calculated according Algorithm A (ISO 13528:2020-09)
- Only EU and EFTA countries laboratories

Statistical Parameters

Results excluded from the population used for robust statistics:

→ **United Kingdom and North Macedonia as non-EU/EFTA countries**

→ **1 lab:** outlier

submitted results are 10 times above the assigned value (problems confirmed by lab)

→ **1 lab for analytes bixafen, diazinon, parathion-ethyl, pyrazophos and quintozene:**

submitted 0.01 mg/kg as a qualitative detection substitute

→ **Results of 101 EU/EFTA labs were used for robust statistics**

Results of robust statistic

mandatory

voluntary

Pesticide	Robust mean X* [mg/kg]	Robust RSD [mg/kg]	MRRL [mg/kg]	Number of results (EU/EFTA)	Spike value [mg/kg]	Ratio X* / spike
Cyfluthrin	0.0672	0.0195	0.010	88	0.0800	84%
DDE-pp	0.0361	0.0115	0.010	96	0.0450	80%
Deltamethrin	0.0842	0.0298	0.010	91	0.110	77%
Diazinon	0.0766	0.0107	0.010	92	0.0800	96%
Endrin	0.0279	0.0064	0.005	94	0.0300	93%
Fipronil-sulfone	0.0286	0.0042	0.005	85	0.0300	95%
Lambda-cyhalothrin	0.1418	0.0450	0.010	87	0.185	77%
Lindane	0.0414	0.0092	0.010	97	0.0500	83%
Parathion-ethyl	0.0949	0.0160	0.010	91	0.105	90%
Phoxim	0.1046	0.0145	0.010	69	0.110	95%
Pyrazophos	0.0871	0.0103	0.010	83	0.0900	97%
Quintozene	0.0515	0.0109	0.010	85	0.0750	69%
Bixafen	0.1	0.0131	0.010	63	0.100	100%
Hydroxy-Tebuconazole*	0.1324	0.0169	0.010	16	0.125	106%
Tau-Fluvalinate	0.1013	0.0333	0.010	74	0.145	70%
Thiacloprid	0.0754	0.0071	0.010	69	0.0750	101%

Assigned value > 0.1 mg/kg

Assigned value > 3 x MRRL

*for information only!

False negative results – all labs

	Pesticide	Number of results	False negatives	Not analysed
mandatory	Cyfluthrin	90	6	14
	DDE-pp	99	3	5
	Deltamethrin	94	2	10
	Diazinon	96	4	8
	Endrin	97	2	7
	Fipronil-sulfone	88	5	16
	Lambda-cyhalothrin	89	6	15
	Lindane	100	3	4
	Parathion-ethyl	95	7	9
	Phoxim	71	5	33
	Pyrazophos	86	7	18
	Quintozene	88	5	16
voluntary	Bixafen	66	8	38
	Hydroxy-Tebuconazole*	17	11	87
	Tau-Fluvalinate	76	10	28
	Thiacloprid	71	7	33

*for information only!



55 mandatory false negatives
25 voluntary false negatives

PT AO 15: 175 fn

Webtool challenges as reason for false negatives

10 labs did not select their scope in time (lab code 101-110):

- **all analytes** were selected for being in their scope automatically by webtool
- the labs reported their “correct” scope retrospectively
- **this information is additionally given in the report (for information only)**
- *26 false negative results of mandatory analytes (40%)*
- *32 false negative results of voluntary analytes (89%)*

- **for information non analytical false negative results are marked in purple in the following diagramms**

False positive results

7 laboratories reported 11 tentative false positive results

Pesticide detected	Number	Reported concentrations above the MRRL value [mg/kg] (lab code)
Cypermethrin (sum of isomers)	1	0.0859 (11) ^(x)
HCH-beta	3	0.0668 (40); 0.049 (86); 0.036 (103)
Fenvalerate and Esfenvalerate (Sum of RR/SS and RS/SR isomers)	1	0.0468 (50)
Parathion-methyl	1	0.0845 (50)
Permethrin (sum of isomers)	1	0.0338 (50)
Chlordane-cis	1	0.044 (78)
Chlorobenzilate	1	0.012 (78)
Resmethrin (sum of isomers)	1	0.028 (78)
Aldrin	1	0.0379 (85)

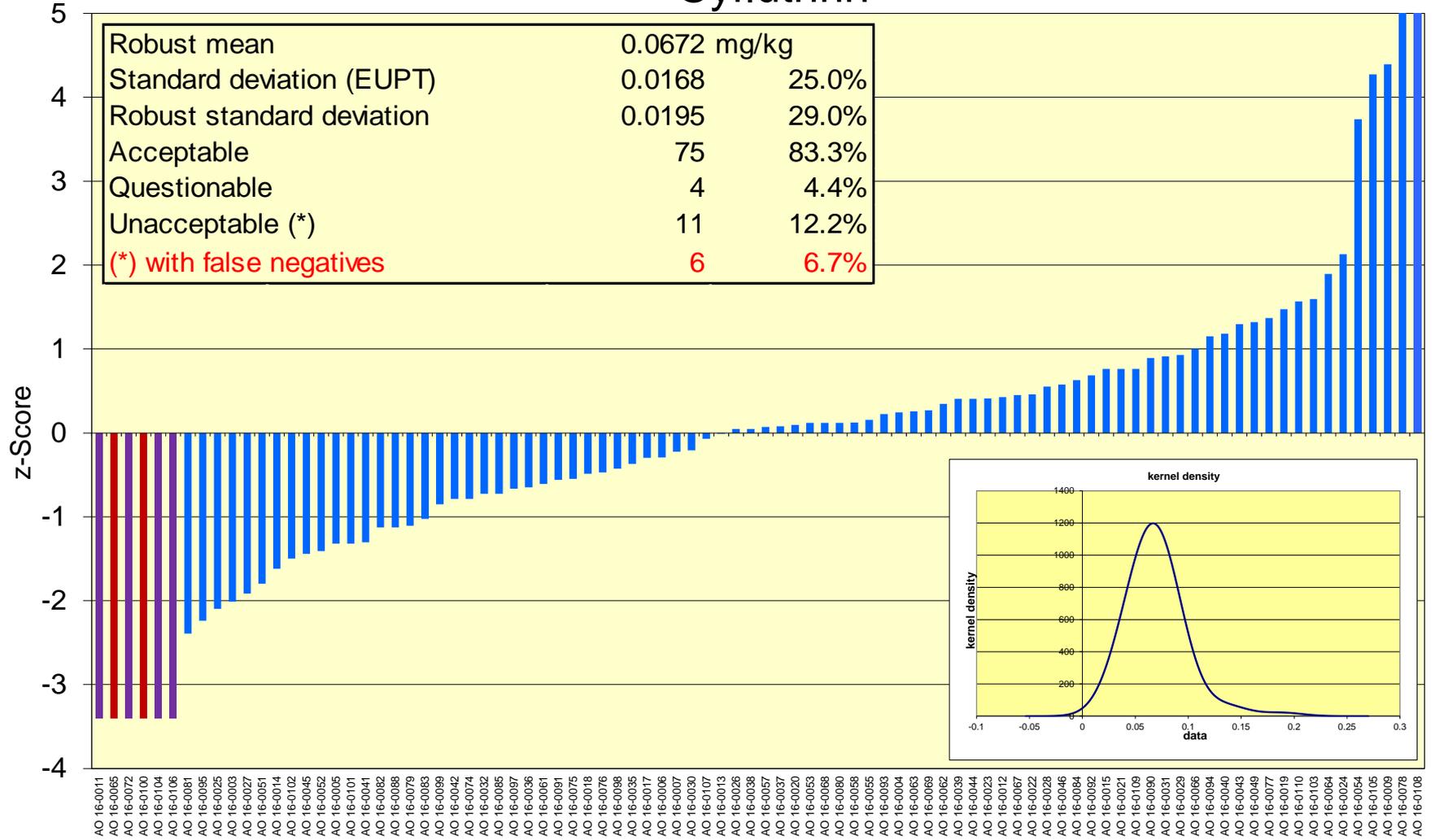
(x) The lab reported that the values applicable to cyfluthrin were submitted as cypermethrin.



A large, faint watermark in the background consisting of the word "EURL" in a blue outline font, surrounded by a circle of twelve yellow stars, similar to the European Union flag.

mandatory pesticides

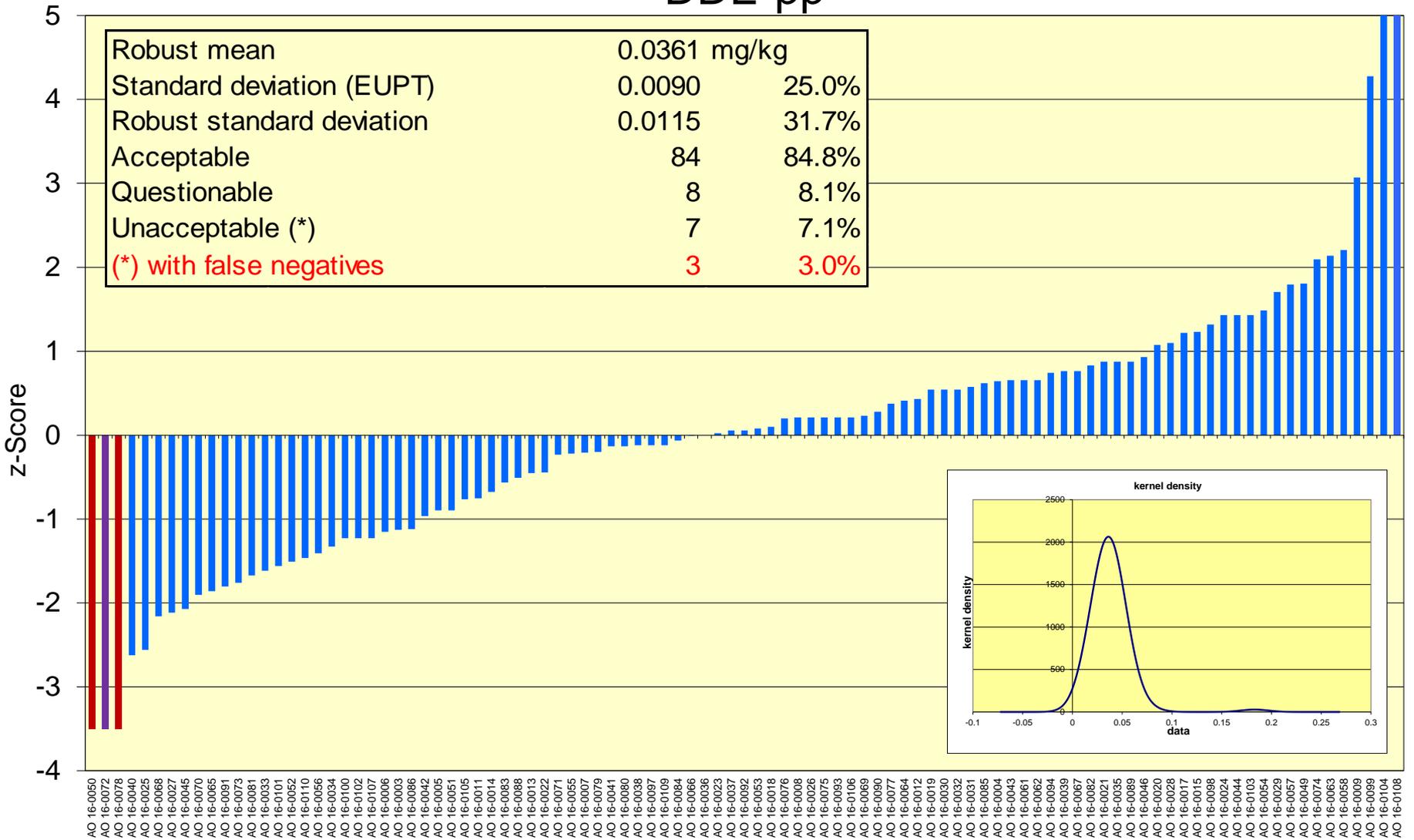
Cyfluthrin



Lab Code

non analytical false negatives

DDE-pp

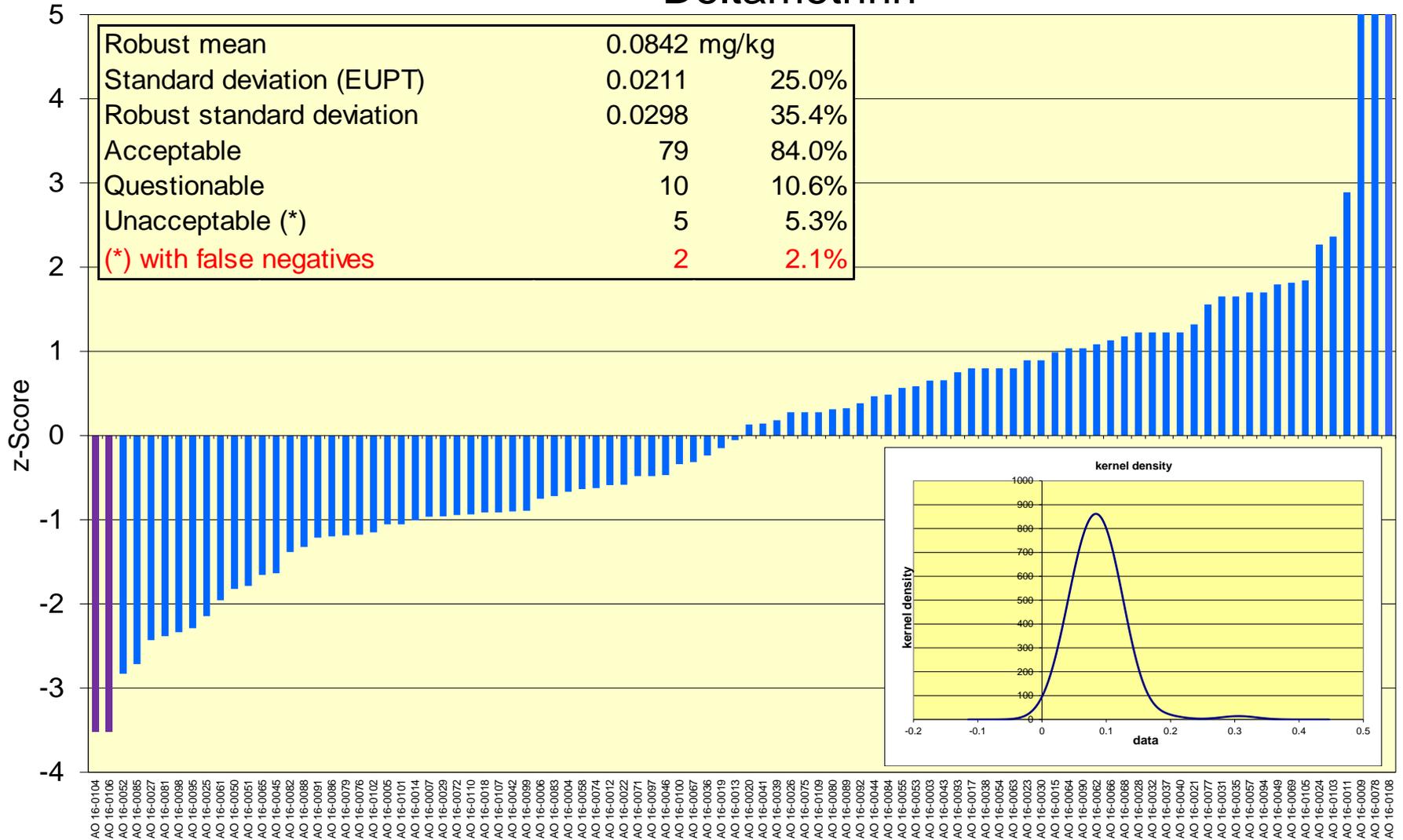


Robust mean	0.0361 mg/kg	
Standard deviation (EUPT)	0.0090	25.0%
Robust standard deviation	0.0115	31.7%
Acceptable	84	84.8%
Questionable	8	8.1%
Unacceptable (*)	7	7.1%
(*) with false negatives	3	3.0%

Lab Code

non analytical false negatives

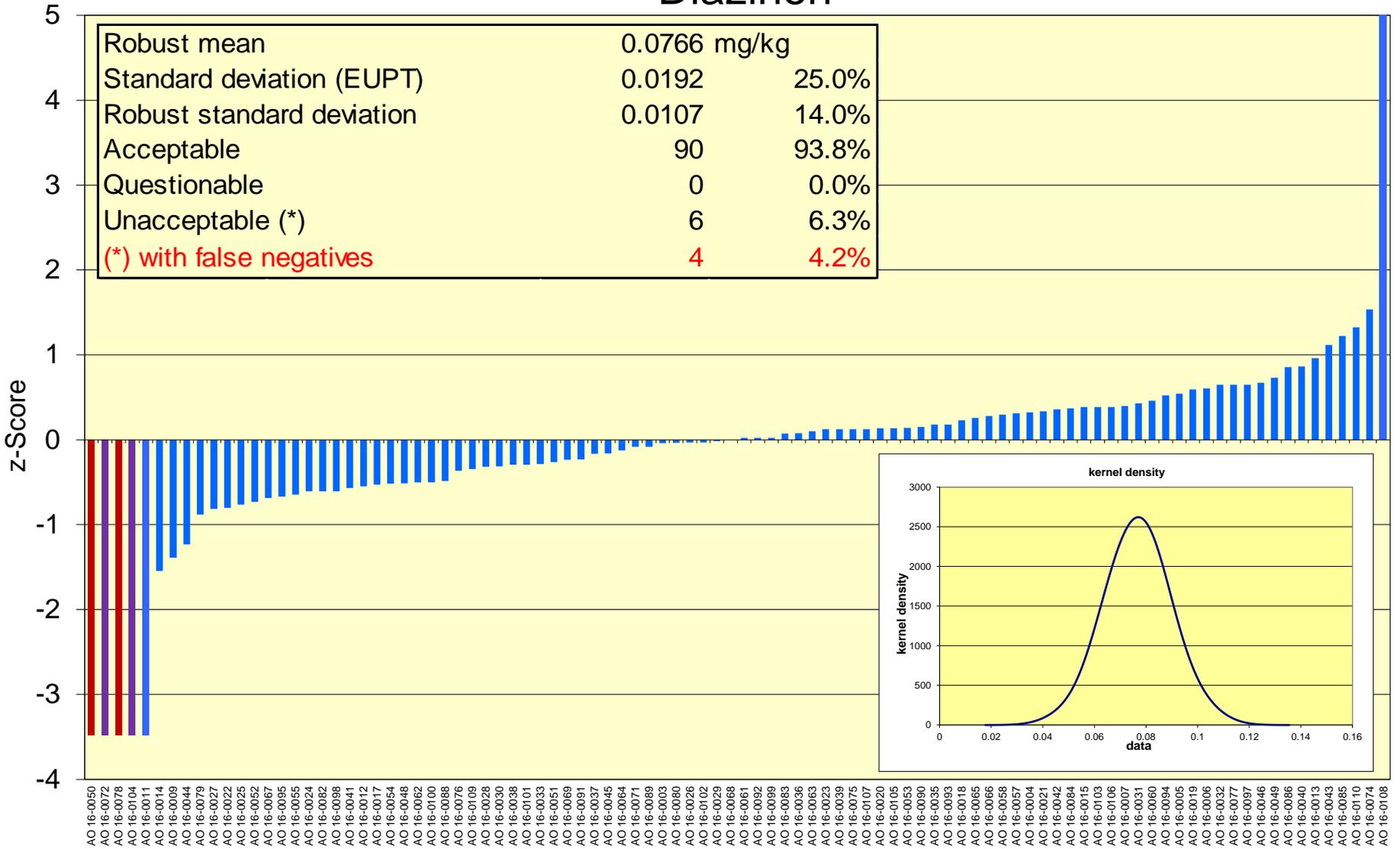
Deltamethrin



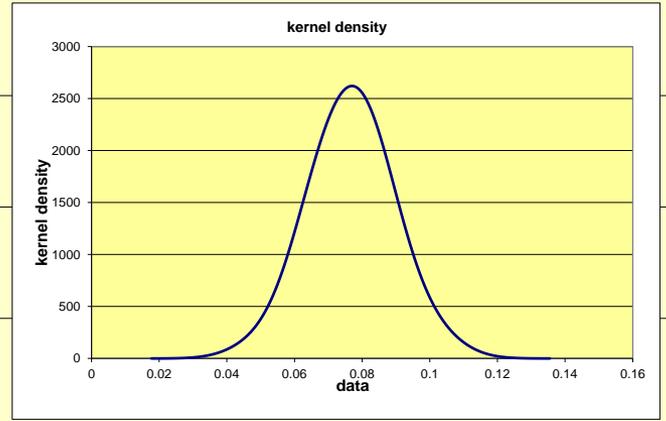
Lab Code

non analytical false negatives

Diazinon



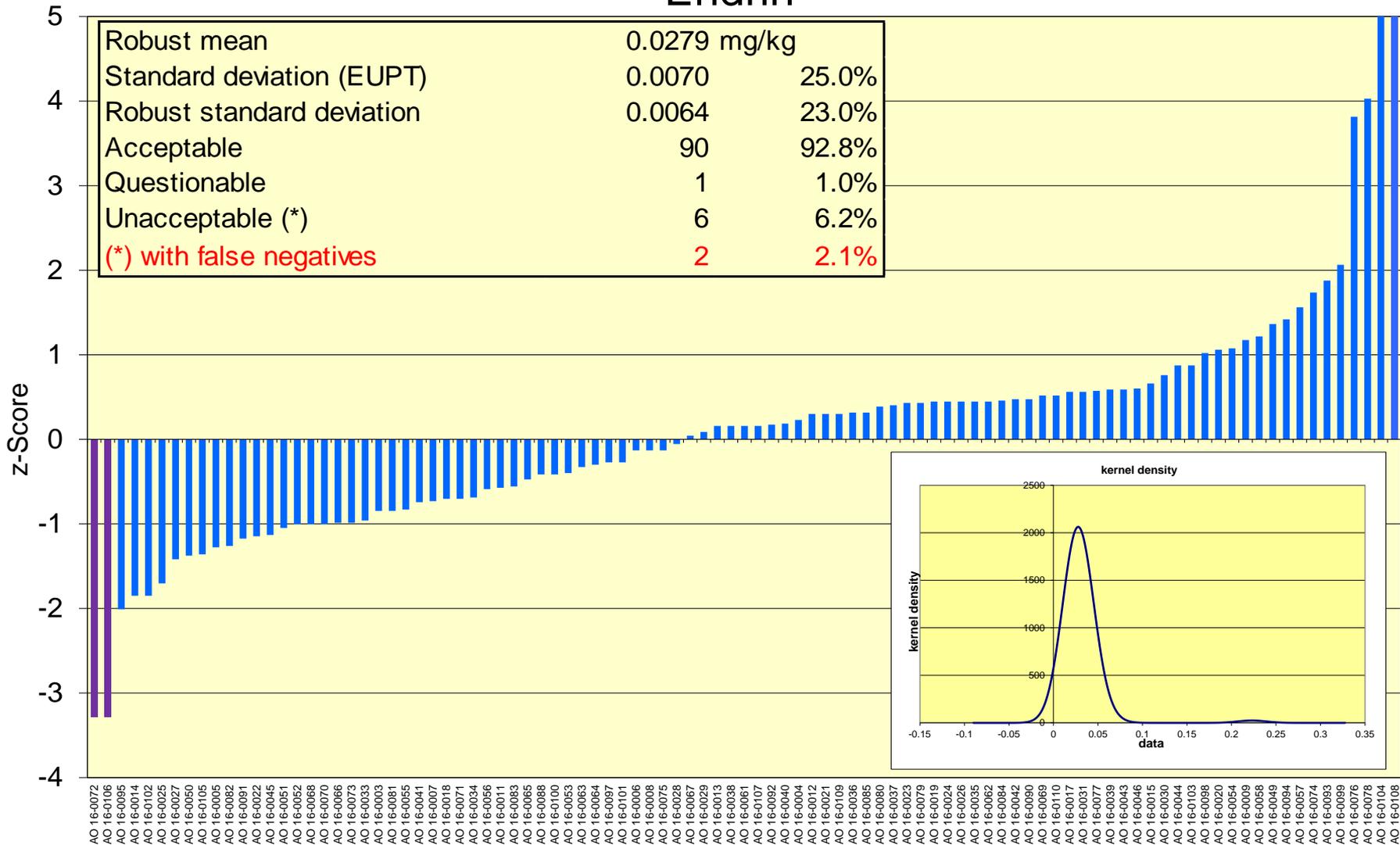
Robust mean	0.0766 mg/kg	
Standard deviation (EUP)	0.0192	25.0%
Robust standard deviation	0.0107	14.0%
Acceptable	90	93.8%
Questionable	0	0.0%
Unacceptable (*)	6	6.3%
(*) with false negatives	4	4.2%



Lab Code

non analytical false negatives

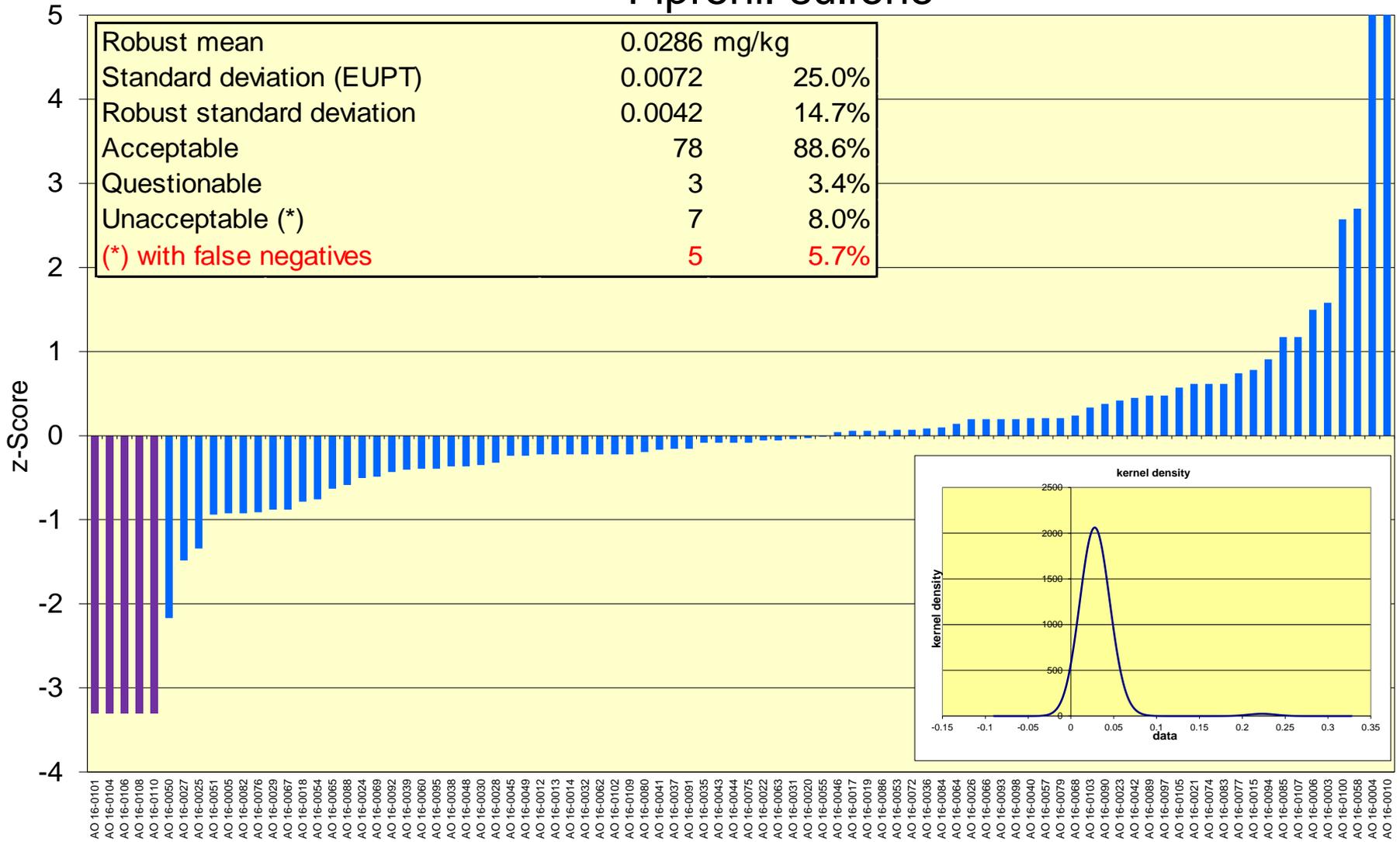
Endrin



Lab Code

non analytical false negatives

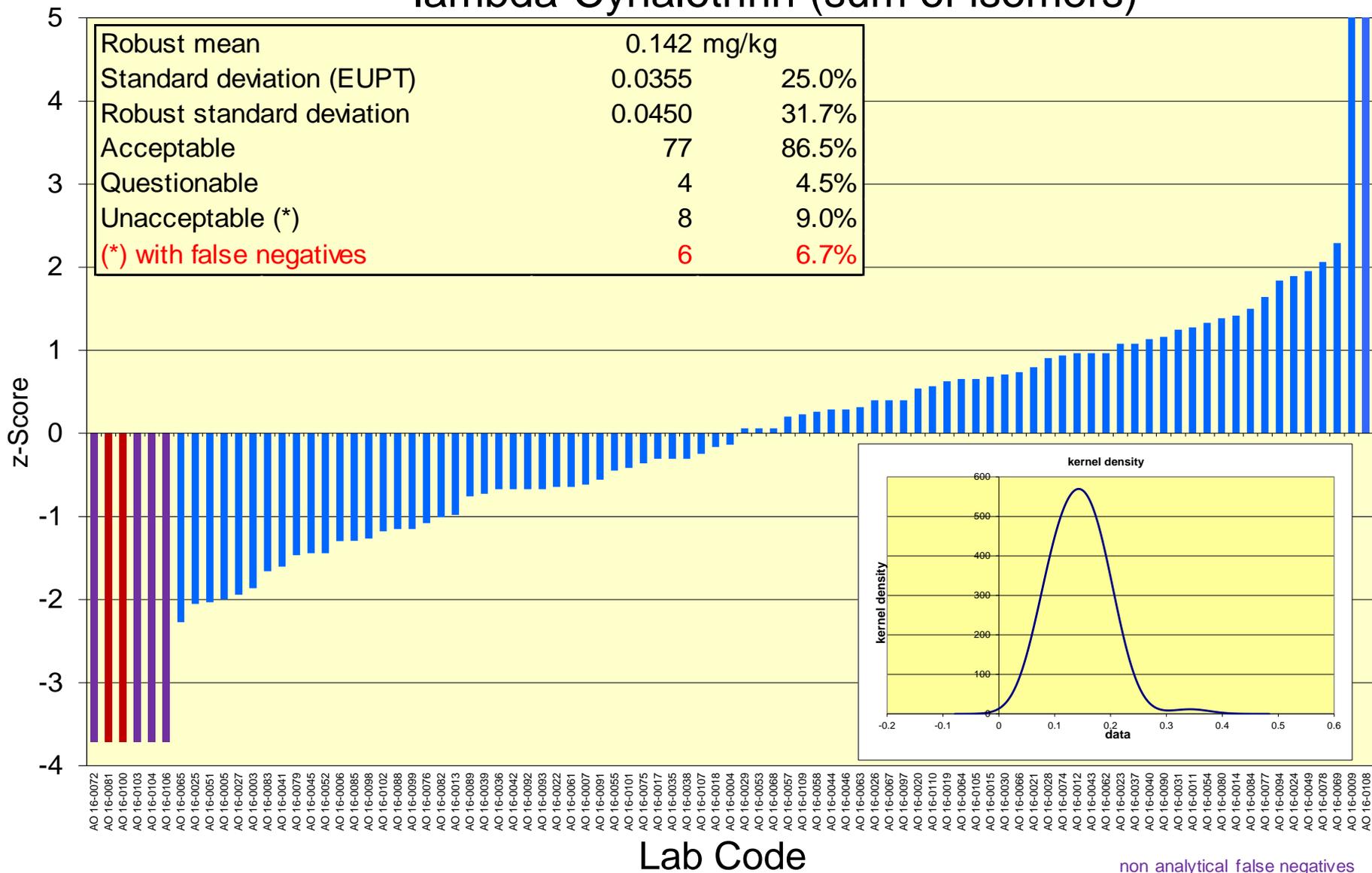
Fipronil-sulfone



Lab Code

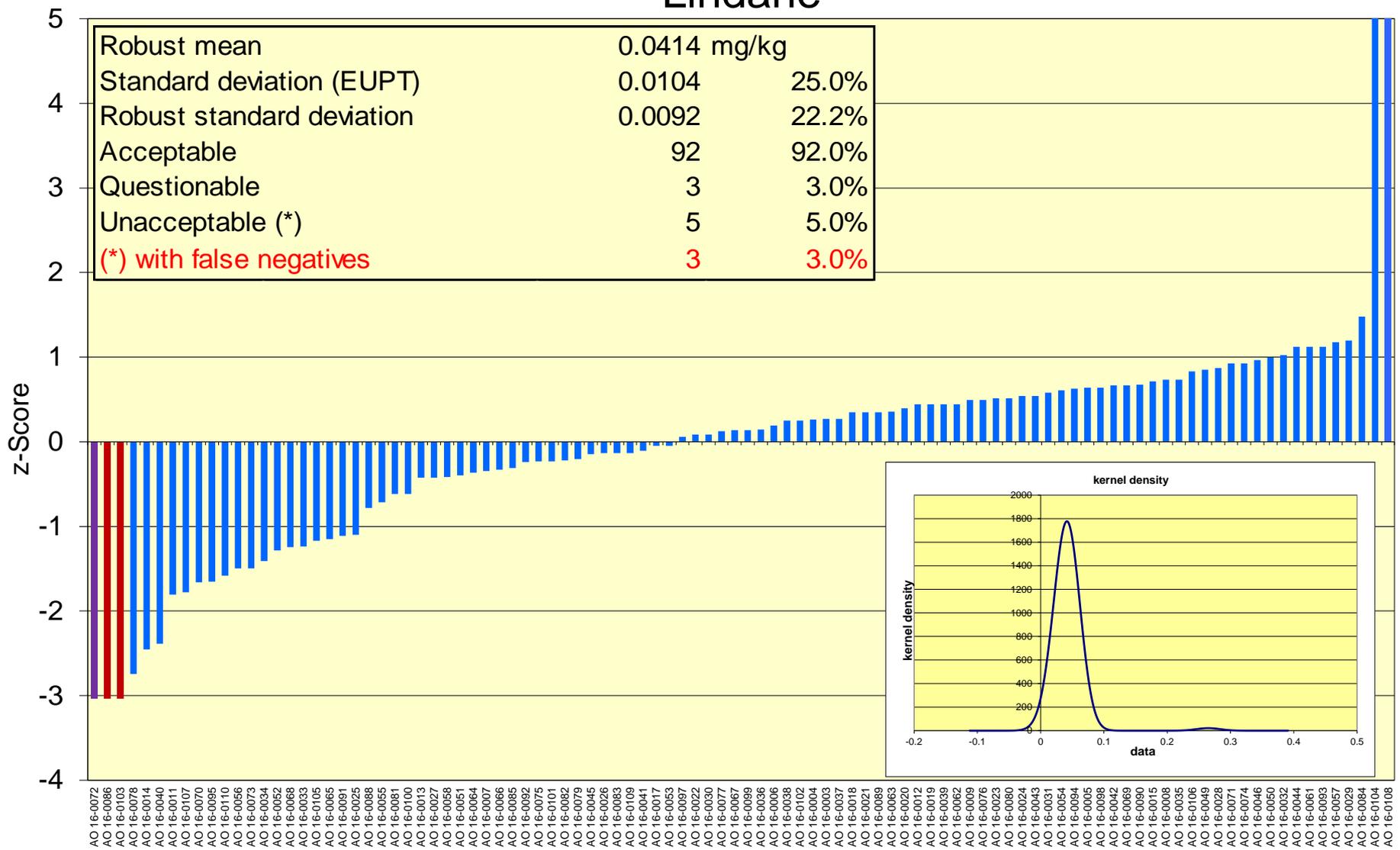
non analytical false negatives

lambda-Cyhalothrin (sum of isomers)



non analytical false negatives

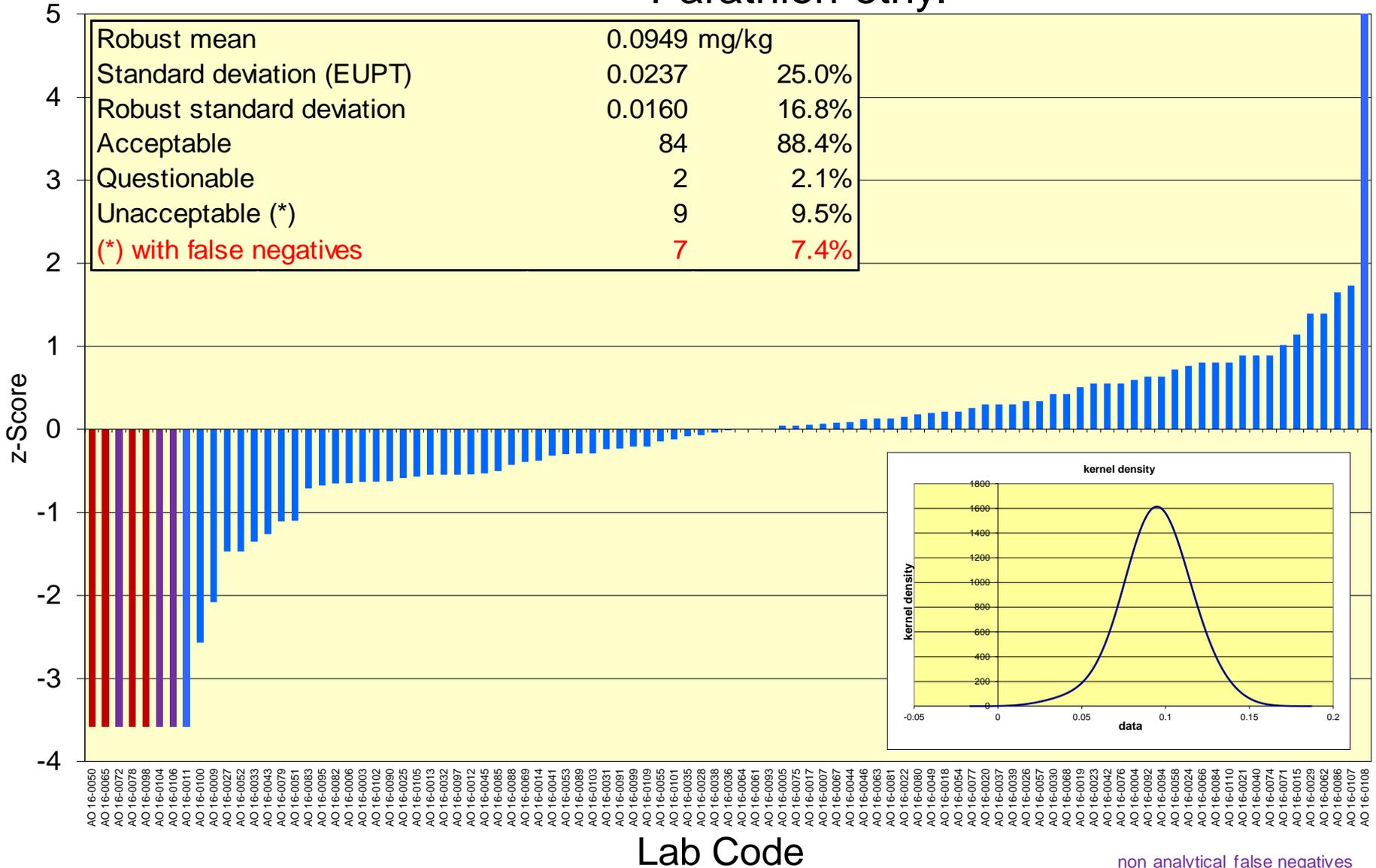
Lindane



Lab Code

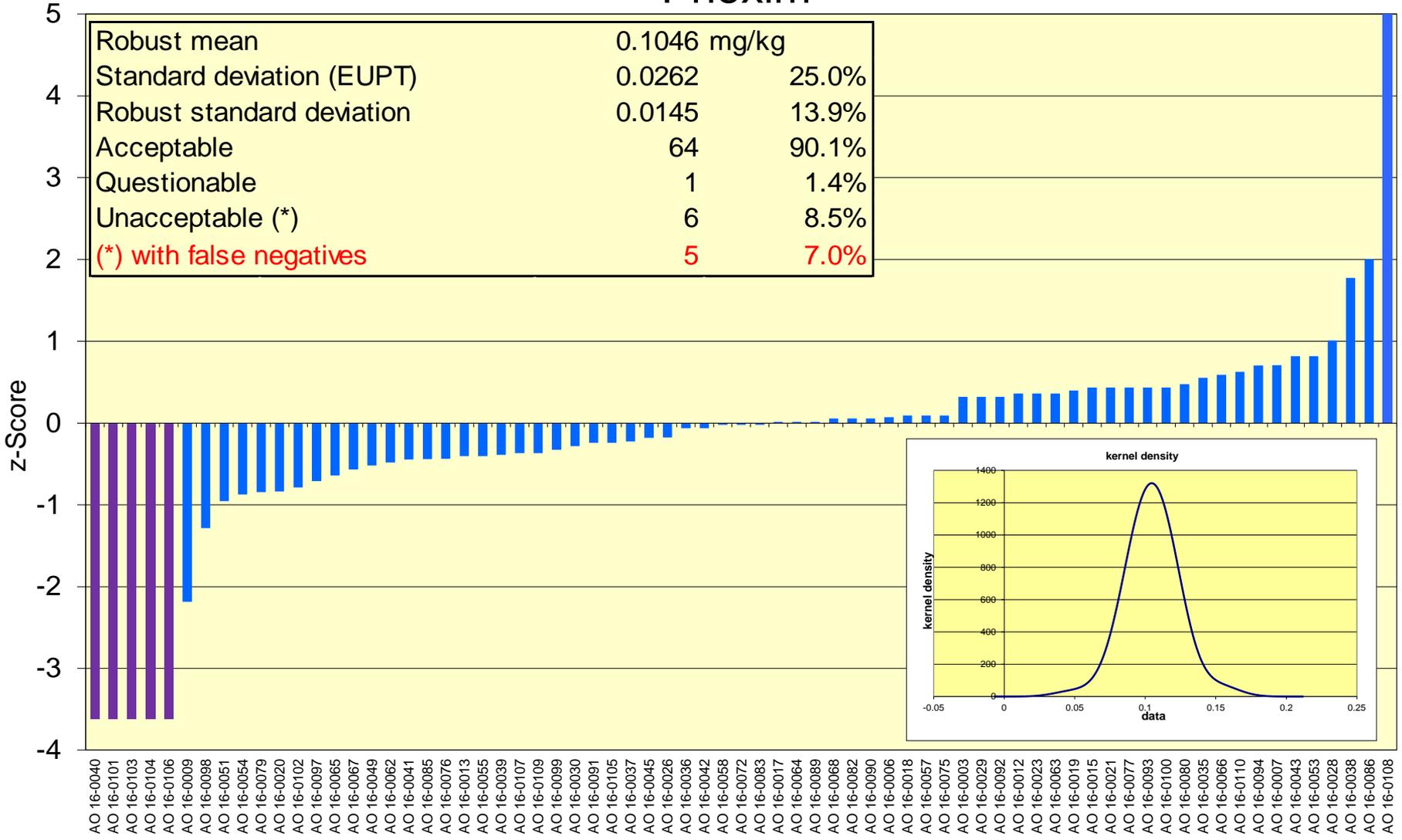
non analytical false negatives

Parathion-ethyl



non analytical false negatives

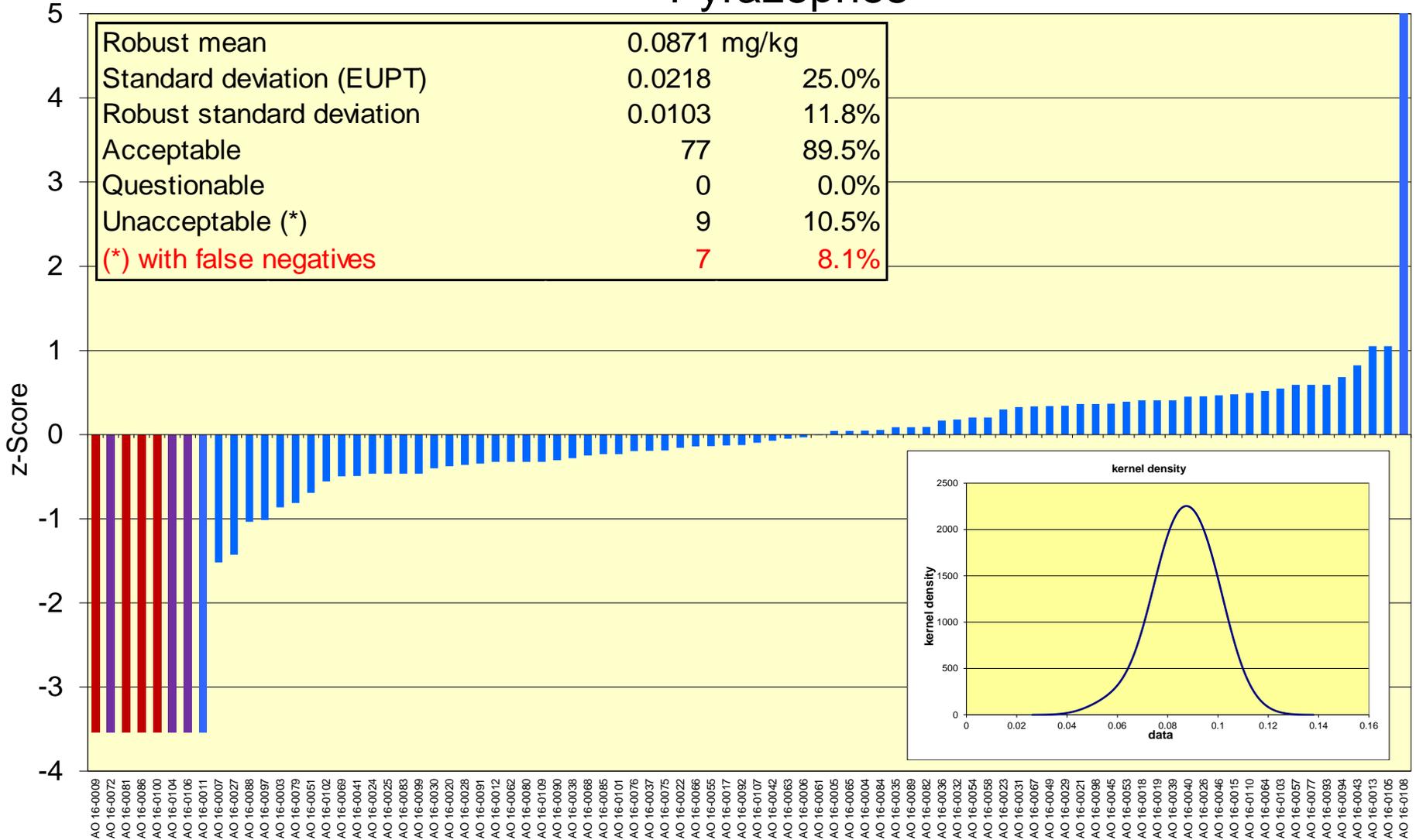
Phoxim



Lab Code

non analytical false negatives

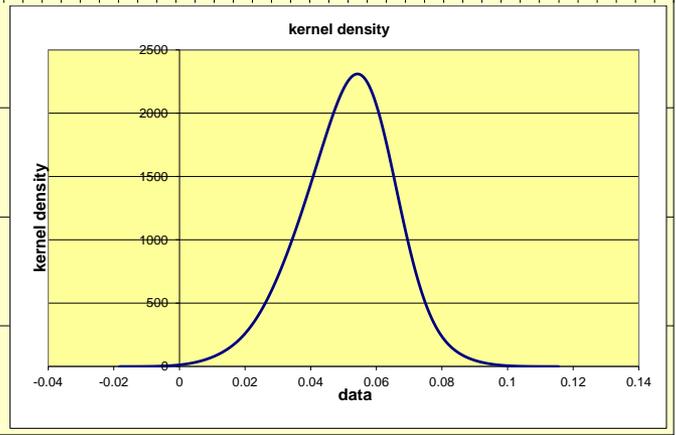
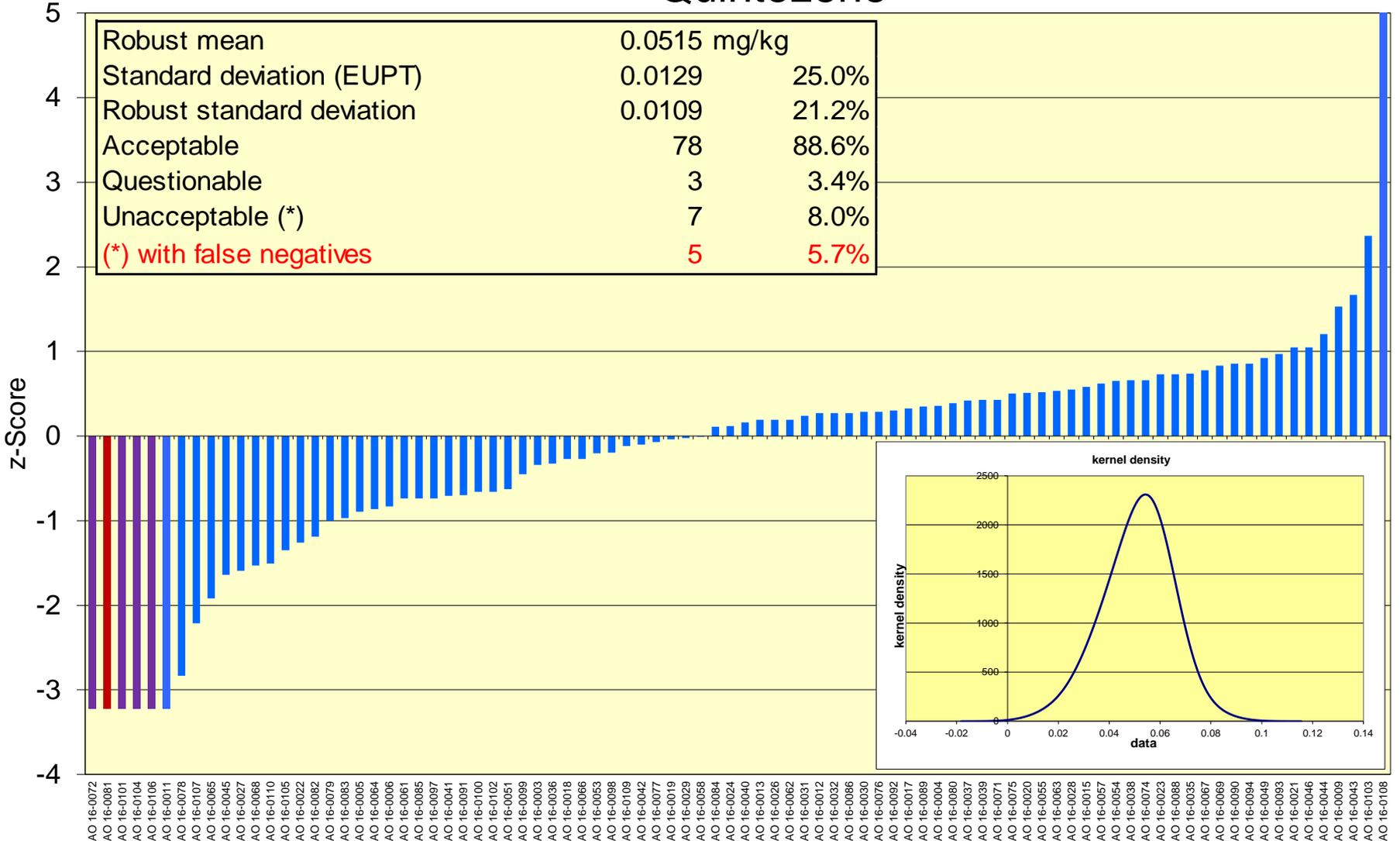
Pyrazophos



Lab Code

non analytical false negatives

Quintozene



Lab Code

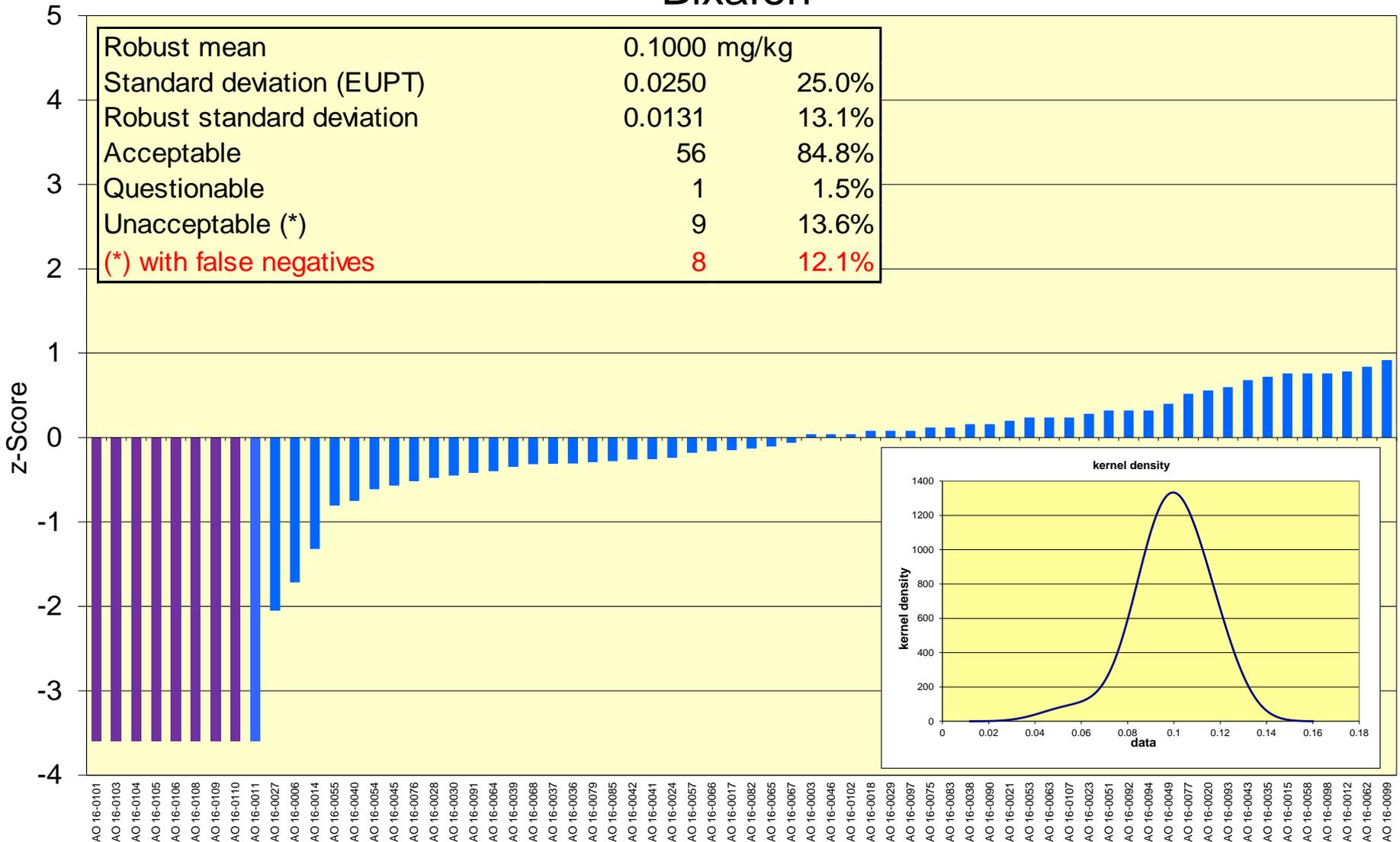
non analytical false negatives

A large, faint watermark in the background consisting of the word "EURL" in a blue outline font, surrounded by a circle of twelve yellow stars, similar to the European Union flag.

voluntary pesticides

Bixafen

Robust mean	0.1000 mg/kg	
Standard deviation (EUPT)	0.0250	25.0%
Robust standard deviation	0.0131	13.1%
Acceptable	56	84.8%
Questionable	1	1.5%
Unacceptable (*)	9	13.6%
(*) with false negatives	8	12.1%



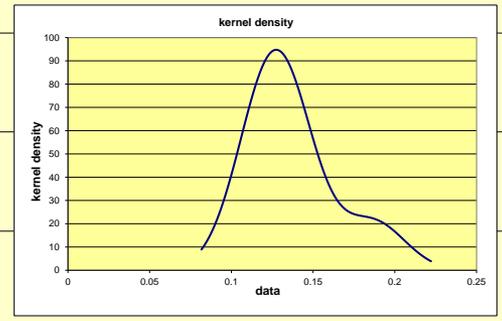
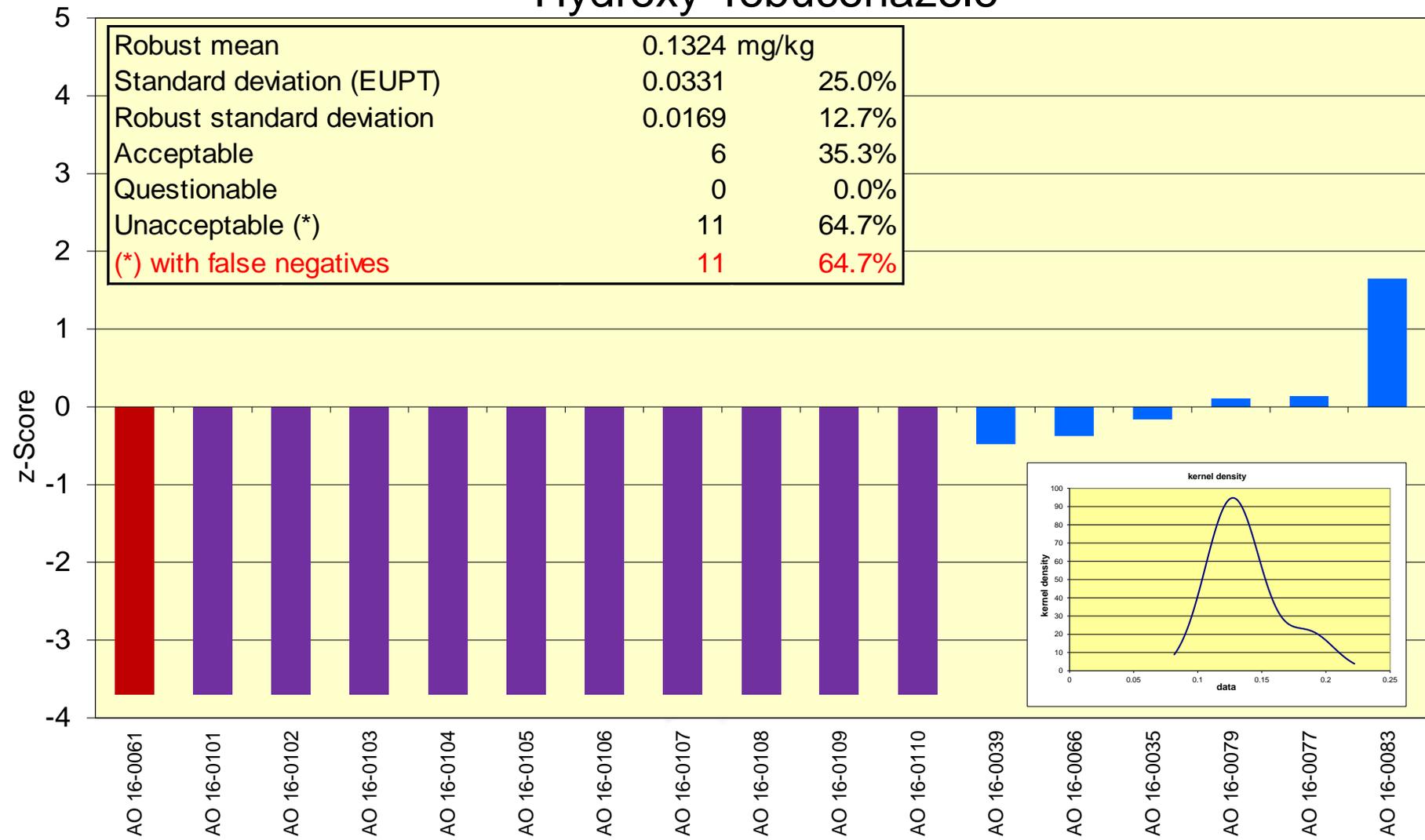
Lab Code

non analytical false negatives

For information only!

Hydroxy-Tebuconazole

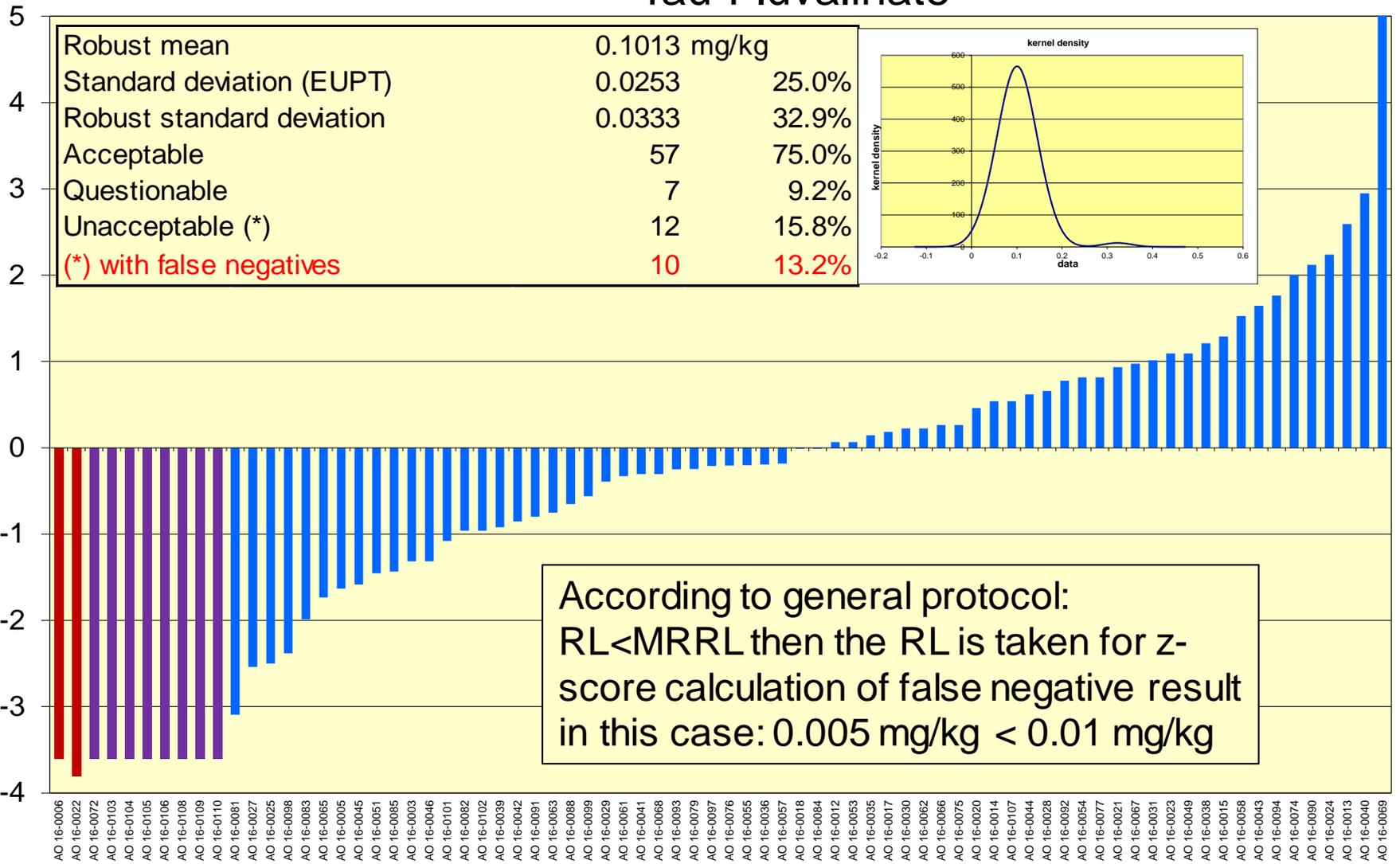
Robust mean	0.1324 mg/kg	
Standard deviation (EUPT)	0.0331	25.0%
Robust standard deviation	0.0169	12.7%
Acceptable	6	35.3%
Questionable	0	0.0%
Unacceptable (*)	11	64.7%
(*) with false negatives	11	64.7%



Lab Code

non analytical false negatives

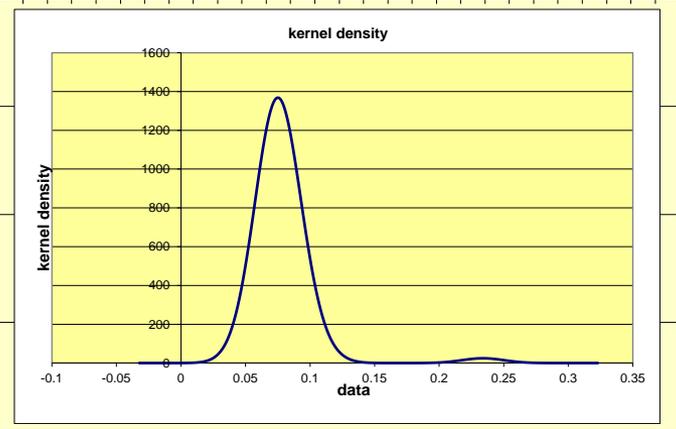
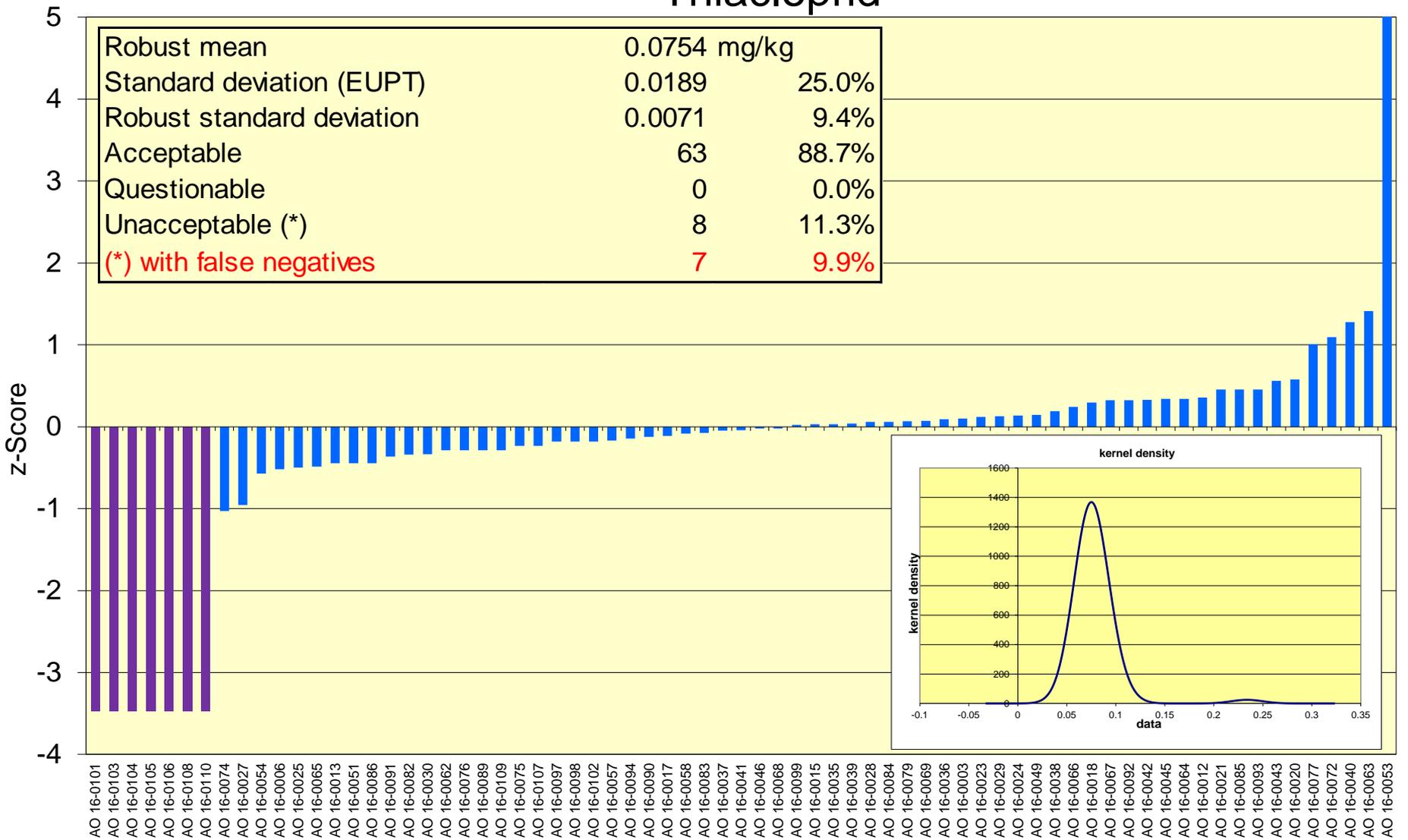
Tau-Fluvalinate



Lab Code

non analytical false negatives

Thiacloprid



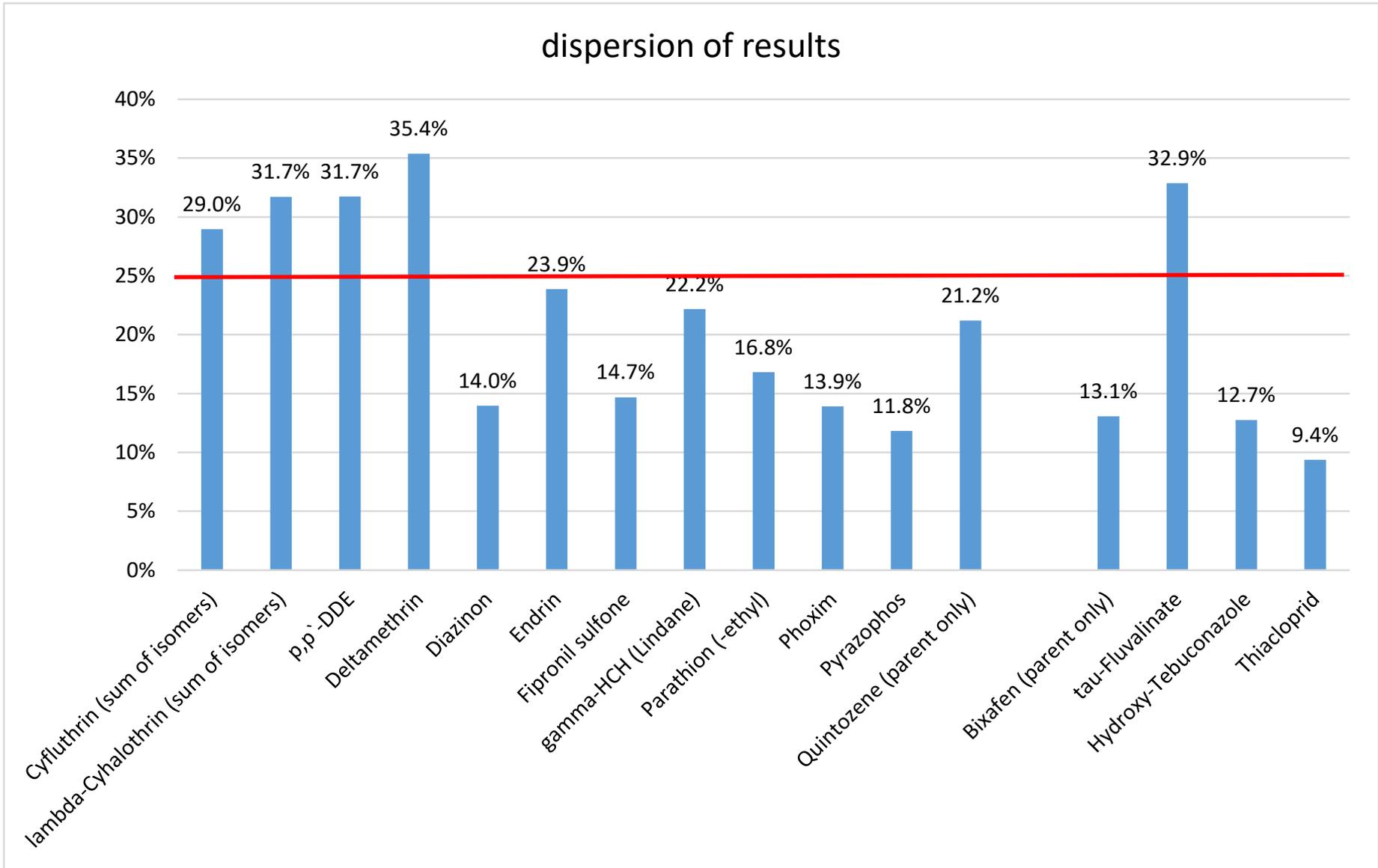
Lab Code

non analytical false negatives

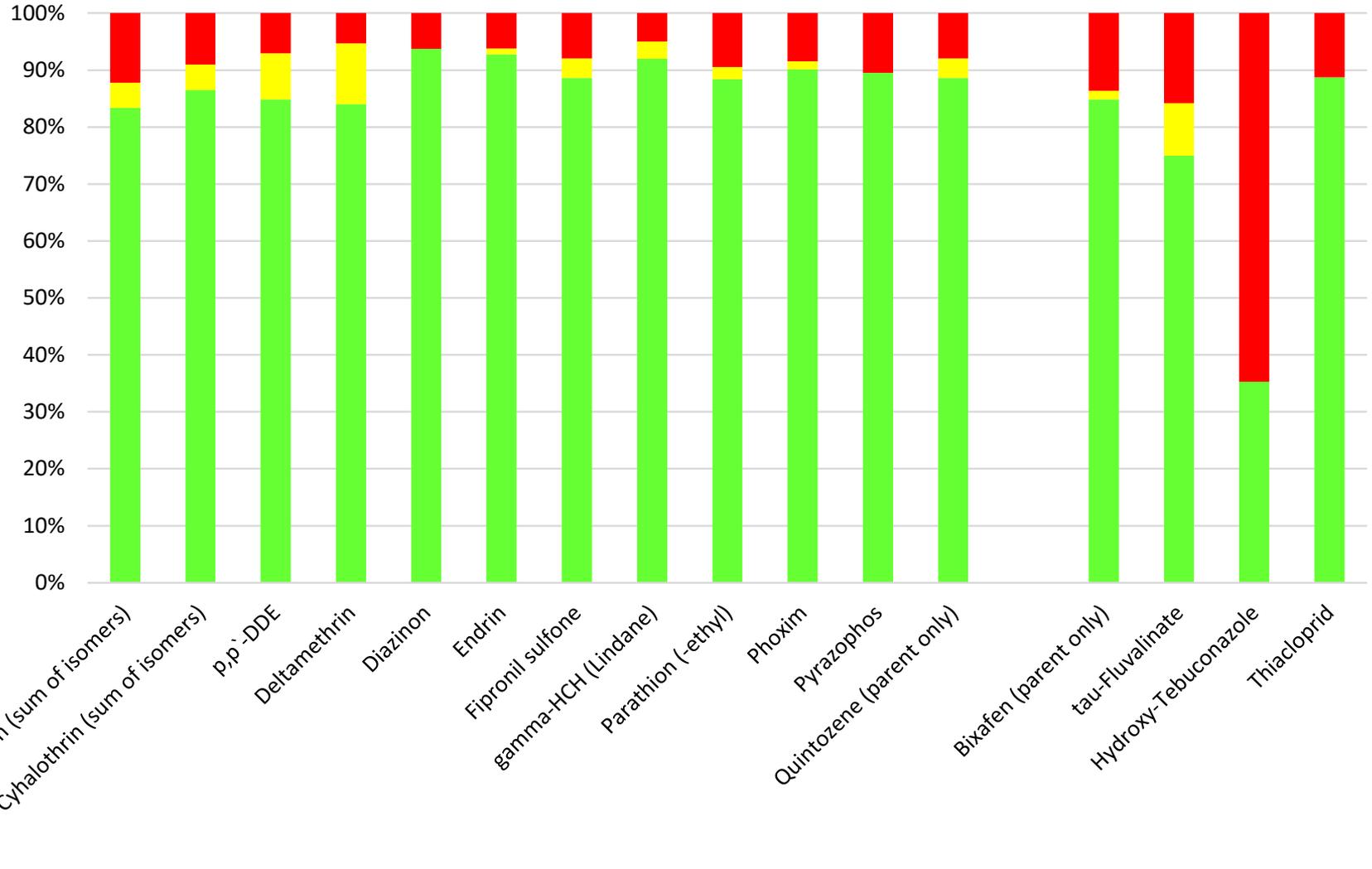
Results

Analyte	Robust mean X* [mg/kg]	robust RSD	number of results	Acceptable	Questionable	Unacceptable	False Negatives	Not analysed	Spike value	Ratio X* / spike	Acceptable	Questionable	Unacceptable
Cyfluthrin (sum of isomers)	0.0672	29.0%	90	75	4	11	6	14	0.0800	84%	83.3%	4.4%	12.2%
lambda-Cyhalothrin (sum of isomers)	0.1418	31.7%	89	77	4	8	6	15	0.185	77%	86.5%	4.5%	9.0%
p,p`-DDE	0.0361	31.7%	99	84	8	7	3	5	0.0450	80%	84.8%	8.1%	7.1%
Deltamethrin	0.0842	35.4%	94	79	10	5	2	10	0.110	77%	84.0%	10.6%	5.3%
Diazinon	0.0766	14.0%	96	90	0	6	4	8	0.0800	96%	93.8%	0.0%	6.3%
Endrin	0.0279	23.0%	97	90	1	6	2	7	0.0300	93%	92.8%	1.0%	6.2%
Fipronil sulfone	0.0286	14.7%	88	78	3	7	5	16	0.0300	95%	88.6%	3.4%	8.0%
gamma-HCH (Lindane)	0.0414	22.2%	100	92	3	5	3	4	0.0500	83%	92.0%	3.0%	5.0%
Parathion (-ethyl)	0.0949	16.8%	95	84	2	9	7	9	0.105	90%	88.4%	2.1%	9.5%
Phoxim	0.1046	13.9%	71	64	1	6	5	33	0.110	95%	90.1%	1.4%	8.5%
Pyrazophos	0.0871	11.8%	86	77	0	9	7	18	0.0900	97%	89.5%	0.0%	10.5%
Quintozene (parent only)	0.0515	21.2%	88	78	3	7	5	16	0.0750	69%	88.6%	3.4%	8.0%
Bixafen (parent only)	0.1	13.1%	66	56	1	9	8	38	0.100	100%	84.8%	1.5%	13.6%
tau-Fluvalinate	0.1013	32.9%	76	57	7	12	10	28	0.145	70%	75.0%	9.2%	15.8%
Hydroxy-Tebuconazole	0.1324	12.7%	17	6	0	11	11	87	0.125	106%	35.3%	0.0%	64.7%
Thiacloprid	0.0754	9.4%	71	63	0	8	7	33	0.0750	101%	88.7%	0.0%	11.3%

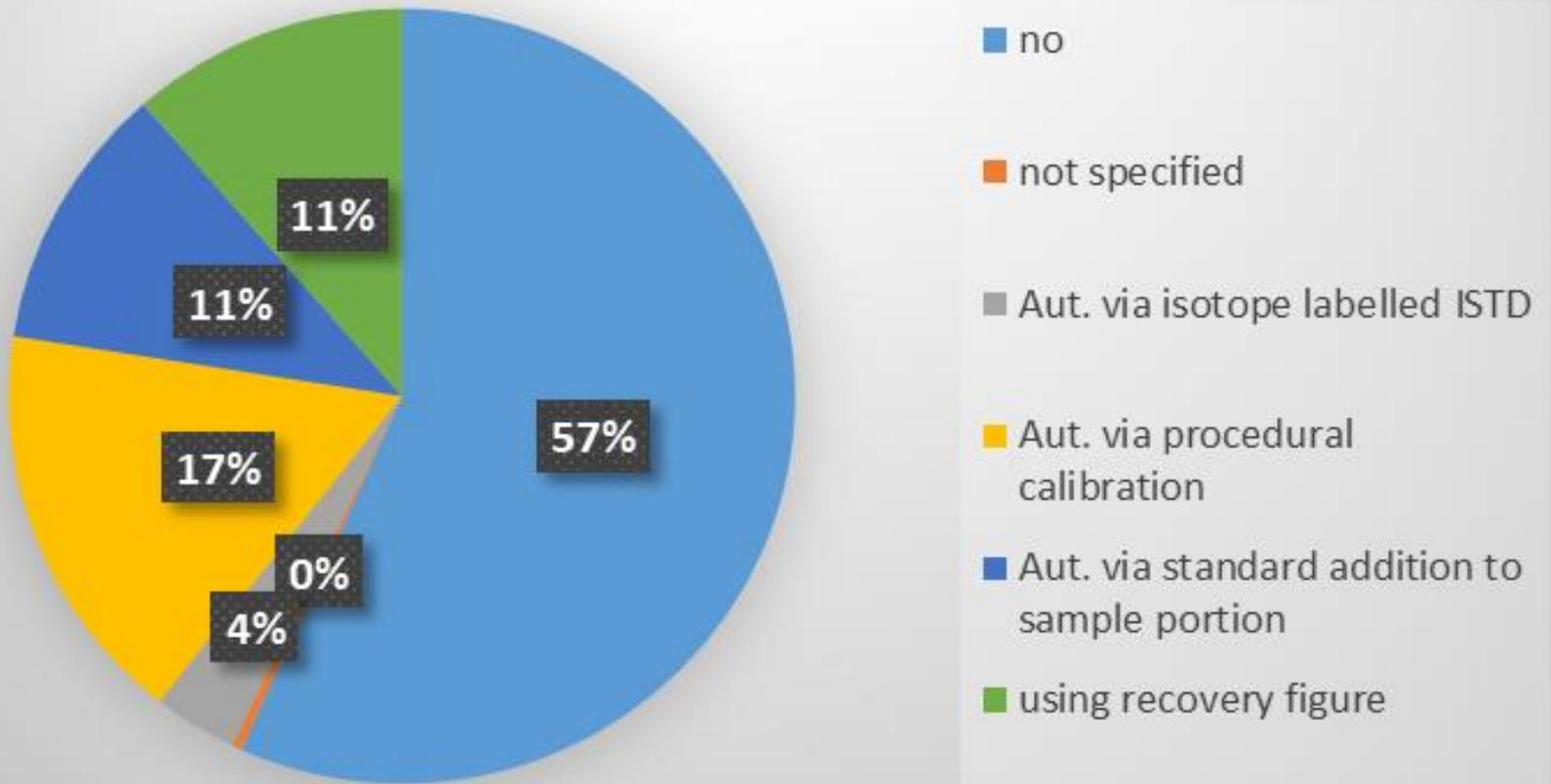
dispersion of results



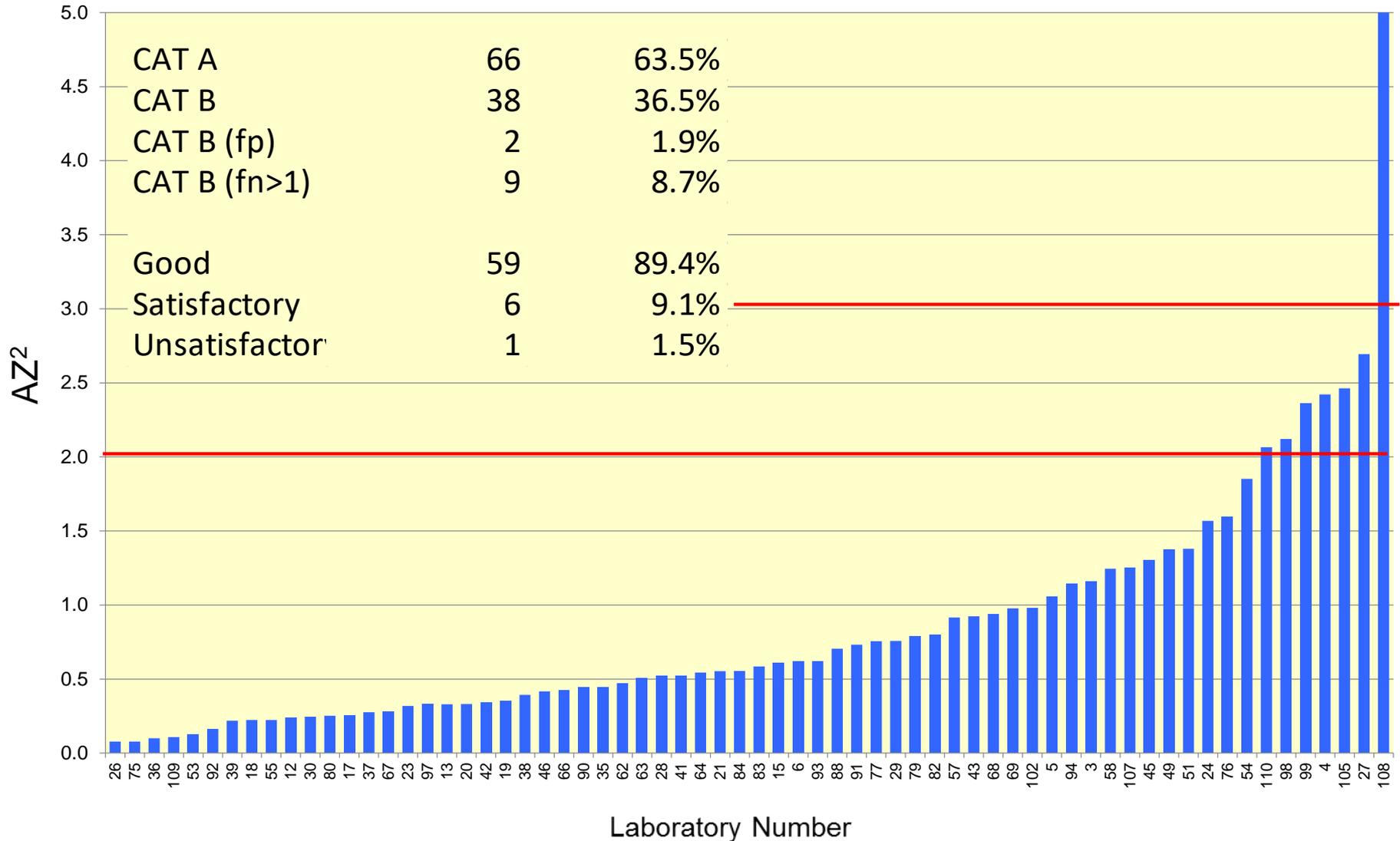
z-scores classification



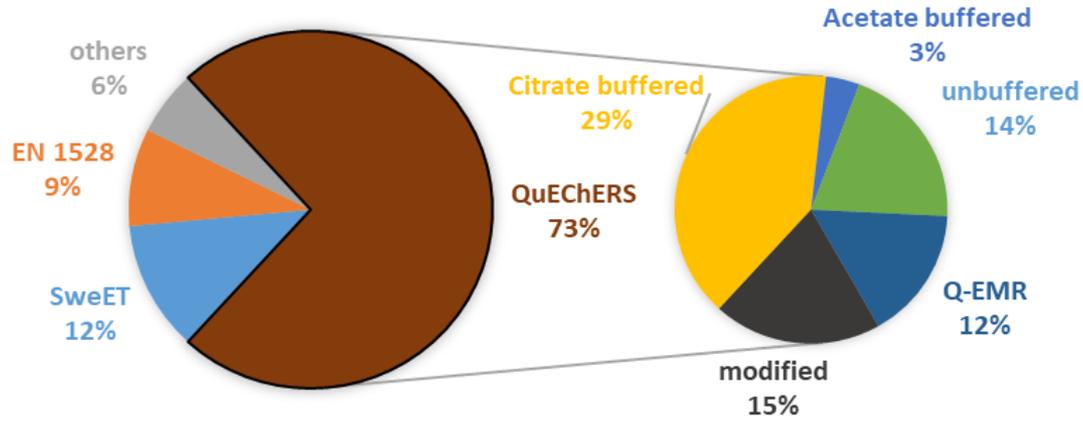
Use of recovery correction of all labs



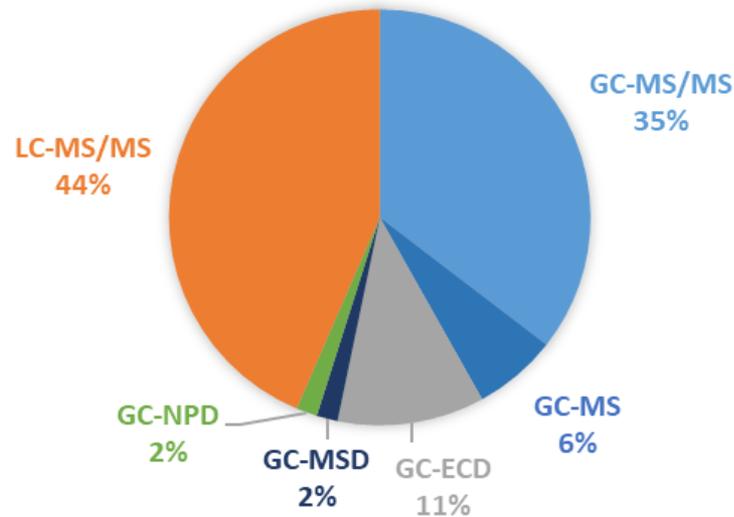
Category A: Average of Squared z-Scores



METHODS USED BY NRLS



DETECTION TECHNIQUES



**Thank You
for Your Attention**



EURL

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