University of Stuttgart
Germany

Analytische Qualitätssicherung Baden-Württemberg

Proficiency Test 4/24
- Pyrethroids in surface water
Bifenthrin, Chlorpyrifos, Chlorpyrifos-methyl, Cypermethrin, Deltamethrin, Fipronil, Lambda-Cyhalotrin, Permethrin, Etofenprox, Tefluthrin

Final report

provided by
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AQS Baden-Württemberg

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on request and in cooperation with
the competence network of the cantonal water protection and environmental protection laboratories of Switzerland, Lab'Eaux

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Version of the report	1.0	

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1. General

This proficiency test was provided by AQS Baden-Württemberg for the determination of bifenthrin, chlorpyrifos, chlorpyrifos-methyl, cyperme-thrin, deltamethrin, fipronil, lambda-cyhalotrin, permethrin, etofenprox and tefluthrin in surface water.

The proficiency test was carried out at the request of and in cooperation with the competence network of the cantonal water protection and environmental protection laboratories of Switzerland, Lab'Eaux. We would like to thank the Intercantonal Laboratory in Schaffhausen for carrying out the analyses for the homogeneity and stability tests.

The PT was executed and evaluated according to the requirements of DIN 38402-A45 and ISO/TS 20612.

2. PT design

Each participant received the following samples:

- 3 samples for the determination of all parameters in 1000-ml glass bottles with screw cap, preservation by cooling

3 different concentration levels/batches were produced. All participants received the same samples.

3. Sample preparation

The samples for the determination of the pyrethroids were based on a real surface water (Bandtälesbach in Stuttgart-Büsnau). The water was filtered with 5µm- and 1µm-filter cartridges.

4. Homogeneity and Stability

The homogeneity and stability of the samples complied with the requirements of ISO 13528:2022-8.

5. Sample distribution

The samples were dispatched on 03.06.2024 by express service.

6. Analytical methods

The participants were free to choose a suitable method, but the following limits of quantification were required:

Parameter	required LOQ
Etofenprox	0,5 ng/l
other parameters	0,05 ng/l

The participants were informed that the samples had to be analysed in the own laboratory, with own personal and own equipment. Subcontracting of the analysis was not allowed.

The samples had to be analysed in duplicate over the complete method (sample preparation and measurement). The participants were asked to report the results as average means from both determinations in ng/l with three significant digits.

7. Submission of the results

The results of the analyses had to be submitted to the organizer via the proficiency testing portal by 24 June 2024. Values received after this date could not be considered.

8. Basic principle of evaluation and assessment

The basic principle of the evaluation and assessment of the PTs from AQS Baden-Württemberg are described in the document „Evaluation of the PTs and information for the report“, which can be downloaded from www.aqsbw.de/pdf/ausw_berichte_v1_en.pdf.

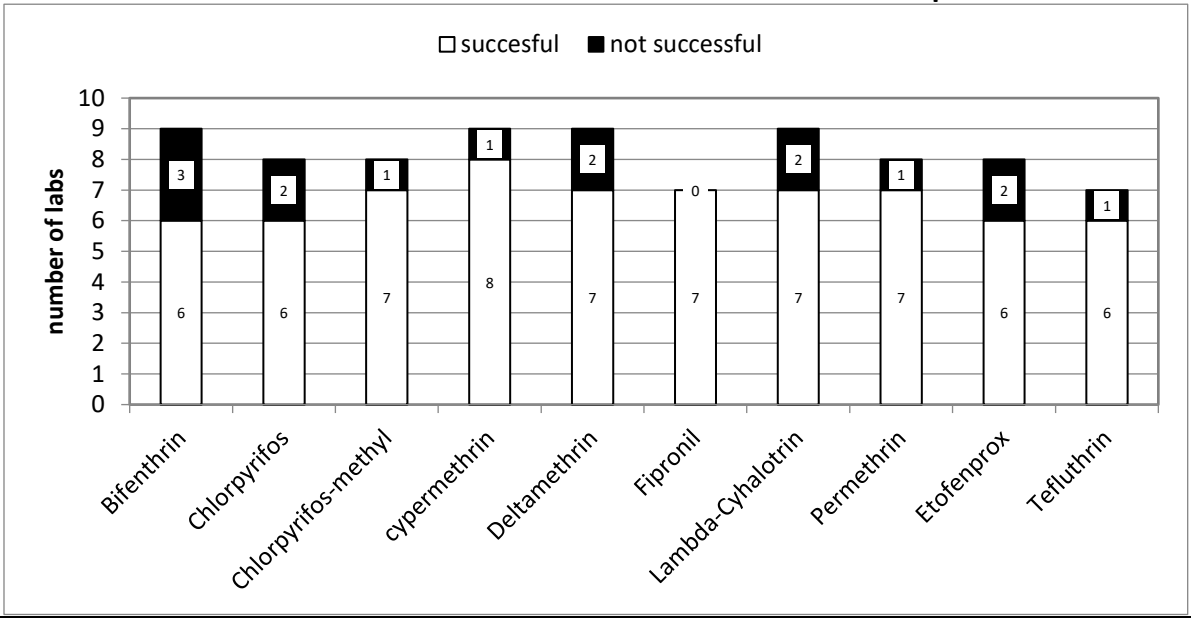
This PT was evaluated as follows:

Assigned value x_{pt}:	Consensus value (Hampel estimator) for all parameters
Standard deviation for proficiency assessment σ_{pt}:	Q method
Upper limit of σ_{pt}:	25 %
Lower limit of σ_{pt}:	5 %
Assessment:	z_U-score
Classification of the single results	$\lvert z_u \rvert \leq 2{,}0$ successful $2{,}0 < \lvert z_u \rvert < 3{,}0$ questionable $\lvert z_u \rvert \geq 3{,}0$ unsatisfactory
Parameter assessment:	A parameter was assessed as successful, if more than half of the values were correctly determined (2 out of 3 values are within the tolerance limits).

9. Evaluation

Number of participants:	14 5 laboratories didn't report results
Number of reported values	246
Number of accepted values:	201 (81,71 %)

Illustration of the susccessful and not successful laboratories for each parameter



10. Explanation for the appendices

The explanations for the appendices can be found in the document „Evaluation of the PTs and information for the report", which can be downloaded from www.aqsbw.de/pdf/ausw_berichte_v1_en.pdf.

In view of the small number of participants, we did not compare methods.

11. Measurement uncertainty (MU)

General:

Number of labs with valid values	9
Number of labs with valid values and reported measurement uncertainties	9 (100 %)
Number of valid values	246
Number of valid values with measurement uncertainties	246 (100 %)

Measurement uncertainties against the accreditation status:

Accreditation status of the values	Number of values	Number of values with measurement uncertainty
accredited	189	189 (100 %)
not accredited	57	57 (100 %)

Interpretation of the reported measurement uncertainties:

In the diagrams showing the measurement uncertainties, it is noticeable that these are often within the realistic range, but some are too small and others are unrealistically large. A plausibility check using the comparative standard deviations in proficiency tests would certainly be helpful here.

If measurement uncertainties are underestimated values assessed as "satisfactory" in the PT ($|z_U| \leq 2$), will have a large ζ -score. $|\zeta| > 2$ means that the "own" requirements (defined in terms of estimated uncertainty) are not fulfilled.

Number of values with reported measurement uncertainty having a $\|z_U\| \leq 2{,}0$	201
Number of values with a magnitude of ζ-scores > 2 The own requirements of the laboratory are not fulfilled and the estimation of the measurement uncertainty is too low	7 (3,5%)

12. Traceable reference values

The explanations about traceable reference values can be found in the document „Evaluation of the PTs and information for the report", which can be downloaded from www.aqsbw.de/pdf/ausw_berichte_v1_en.pdf

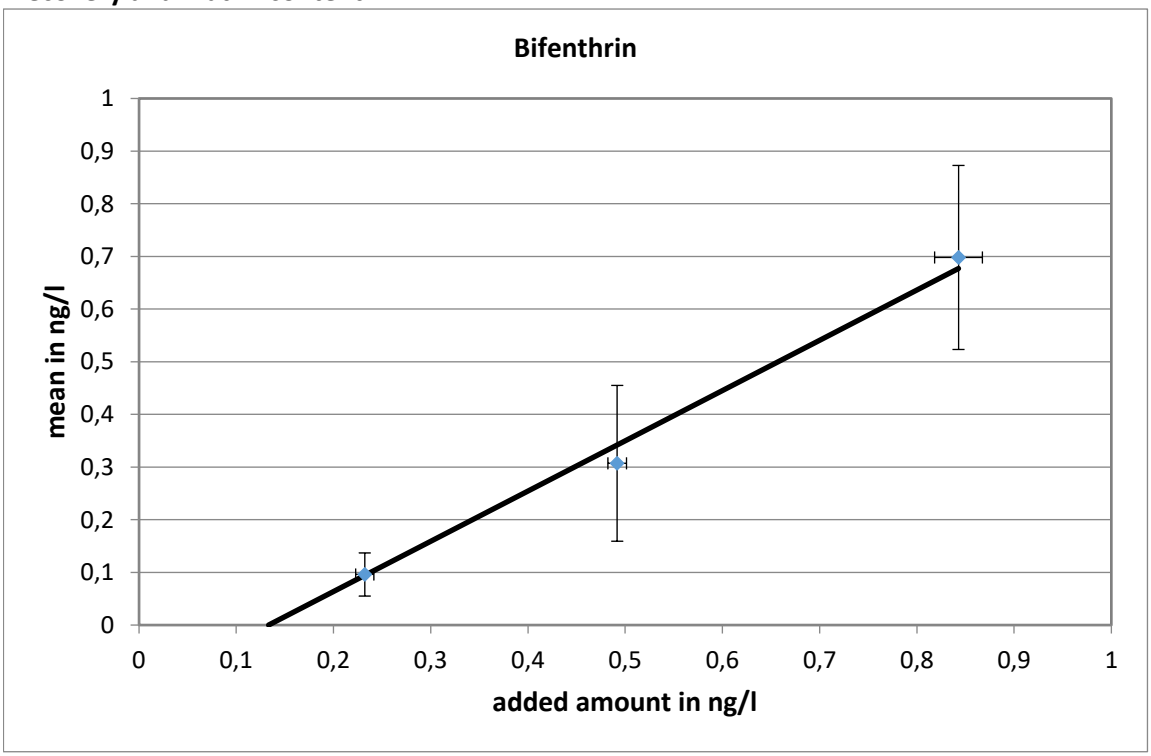
13. Internet

The report is available on the following webpage: www.aqsbw/pdf/305/report_305.pdf

Bifenthrin

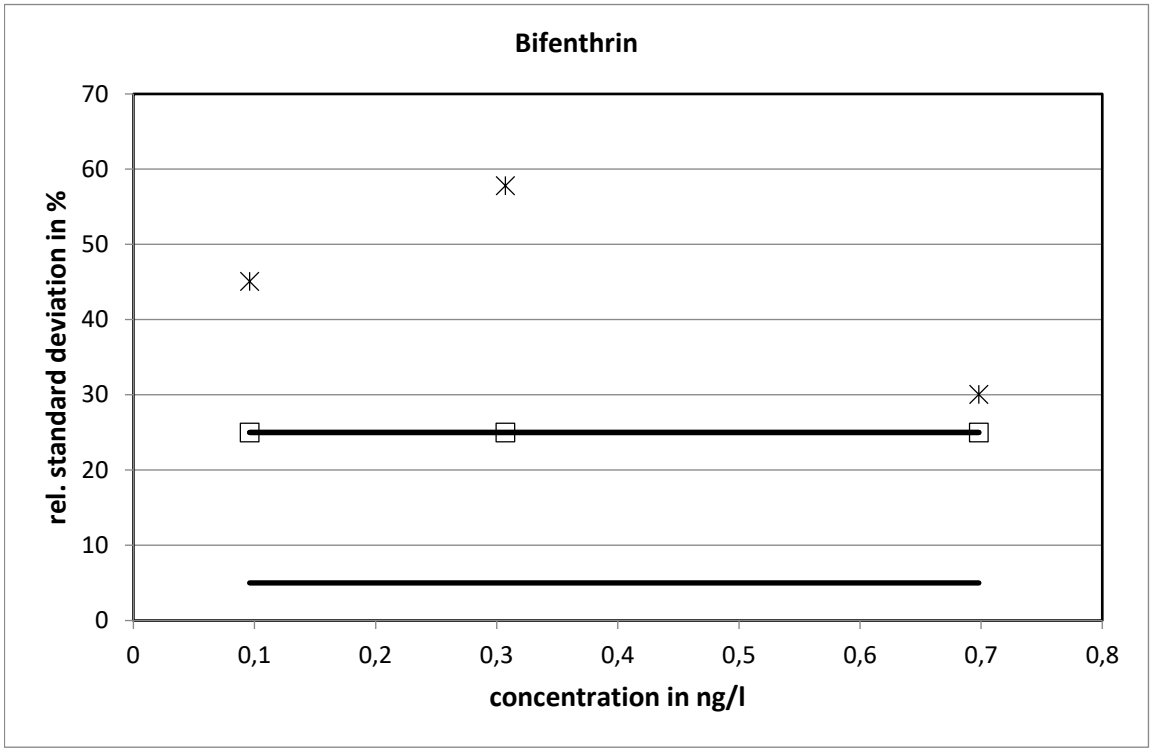
level	assigned value [ng/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [ng/l]	standard deviation for proficiency assessment [ng/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [ng/l]	lower tolerance limit [ng/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,0960	42,60	0,0433	0,0240	25,00	0,1516	0,0526	57,99	-45,19	7	0	3	33,3
2	0,3072	48,16	0,1775	0,0768	25,00	0,4853	0,1684	57,99	-45,19	9	1	1	22,2
3	0,6981	25,03	0,2097	0,1745	25,00	1,103	0,3826	57,99	-45,19	9	0	1	11,1
									sum	25	1	5	24,0

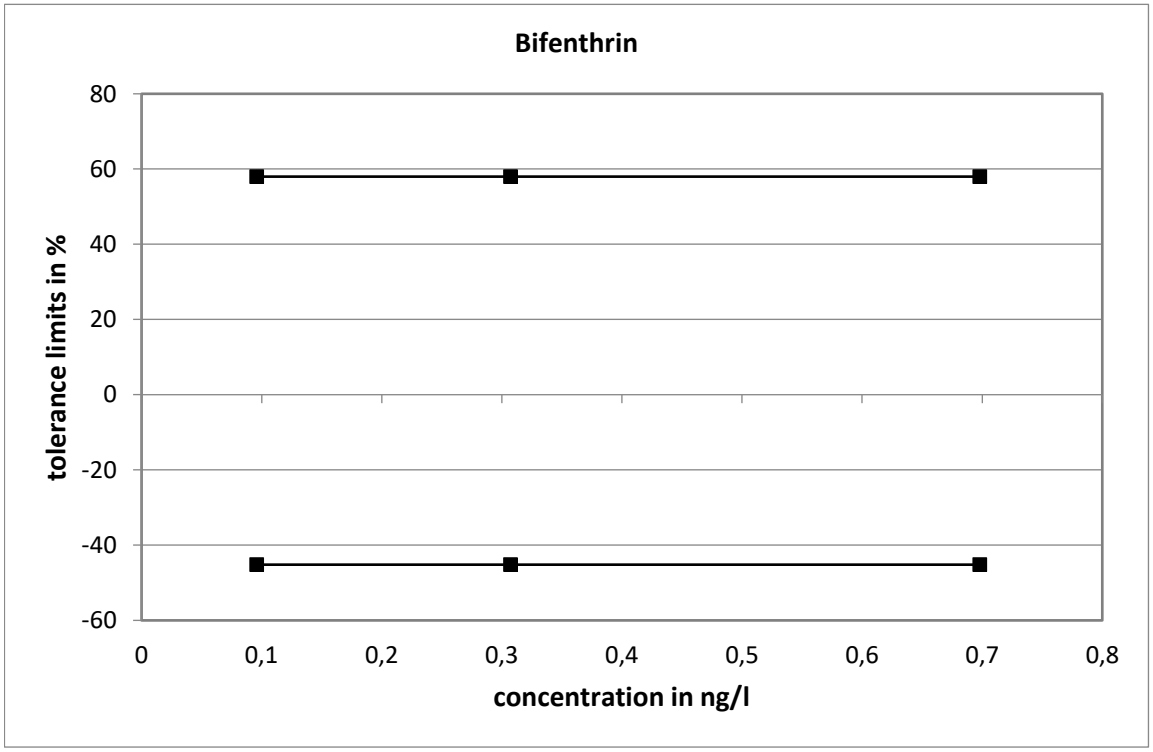
Recovery and matrix content



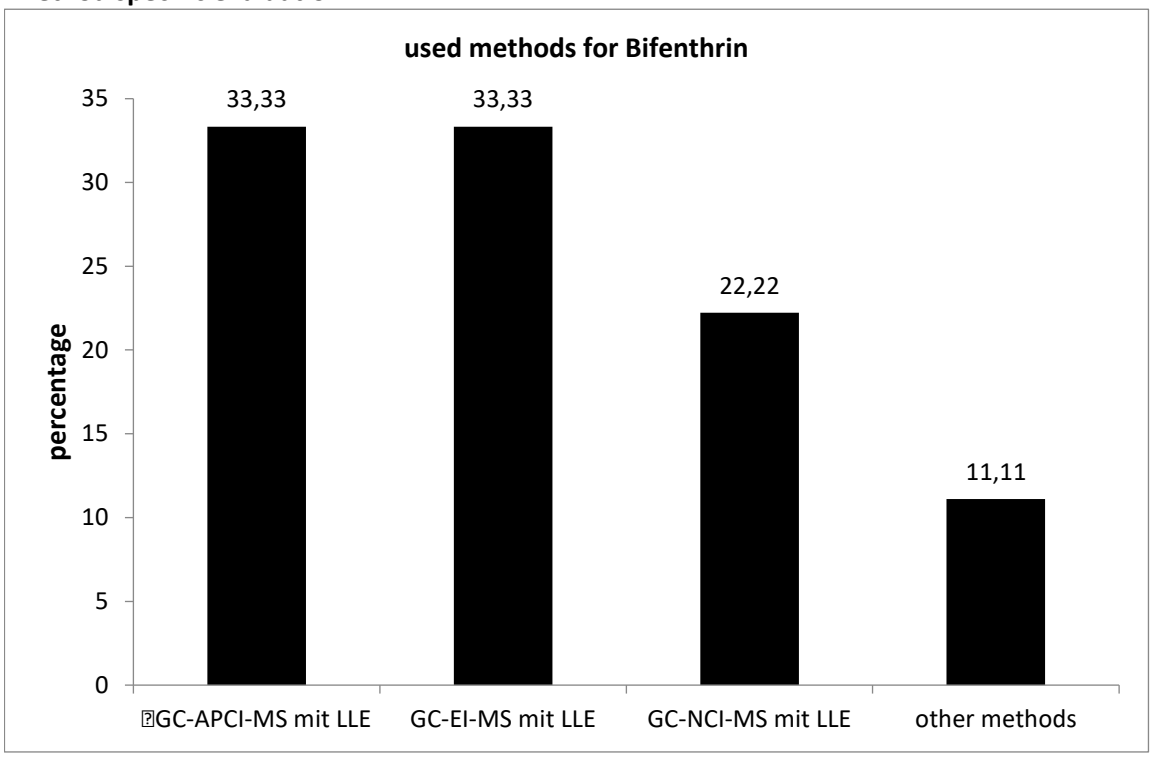
calculated matrix content: 0 ng/l average recovery: 95,4%

Relative standard deviation and tolerance limits





Method specific evaluation

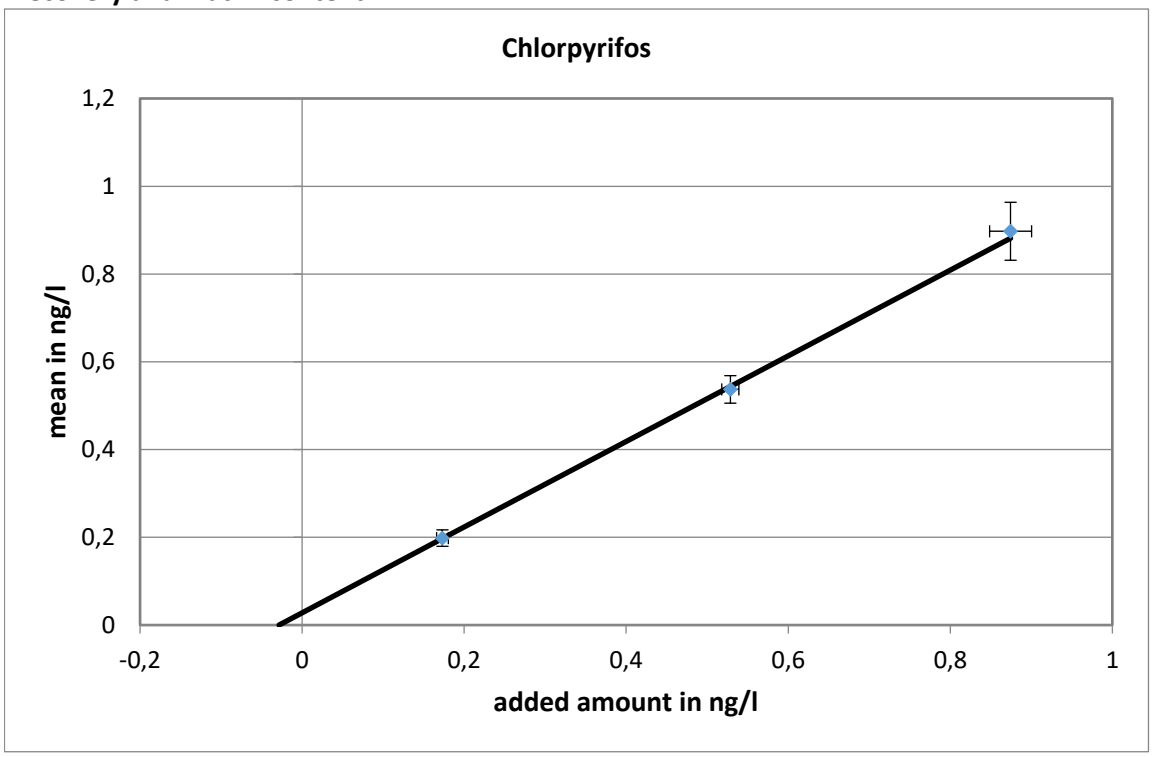


Due to the small number of participants, a comparison of methods is not meaningful.

Chlorpyrifos

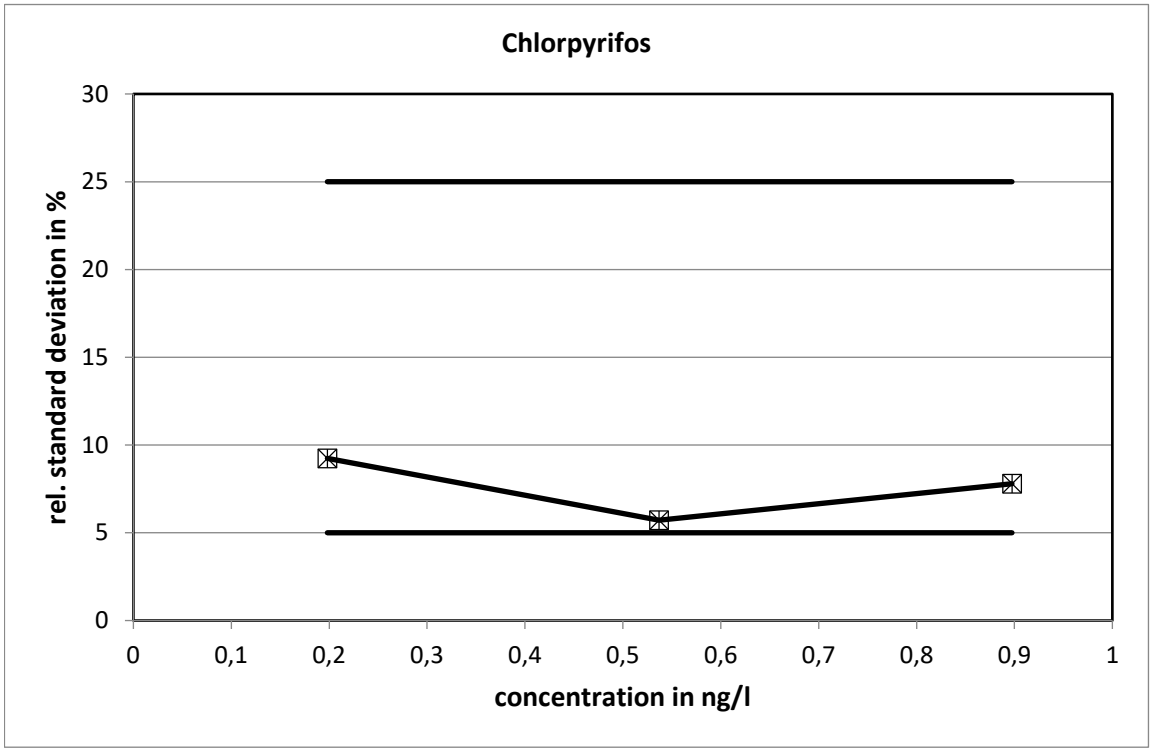
level	assigned value [ng/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [ng/l]	standard deviation for proficiency assessment [ng/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [ng/l]	lower tolerance limit [ng/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,1982	9,43	0,0183	0,0183	9,24	0,2366	0,1631	19,41	-17,70	6	0	2	25,0
2	0,5370	5,83	0,0307	0,0307	5,72	0,6003	0,4773	11,78	-11,13	6	1	1	25,0
3	0,8974	7,36	0,0699	0,0699	7,79	1,043	0,7626	16,23	-15,02	7	0	1	12,5
									sum	19	1	4	26,3

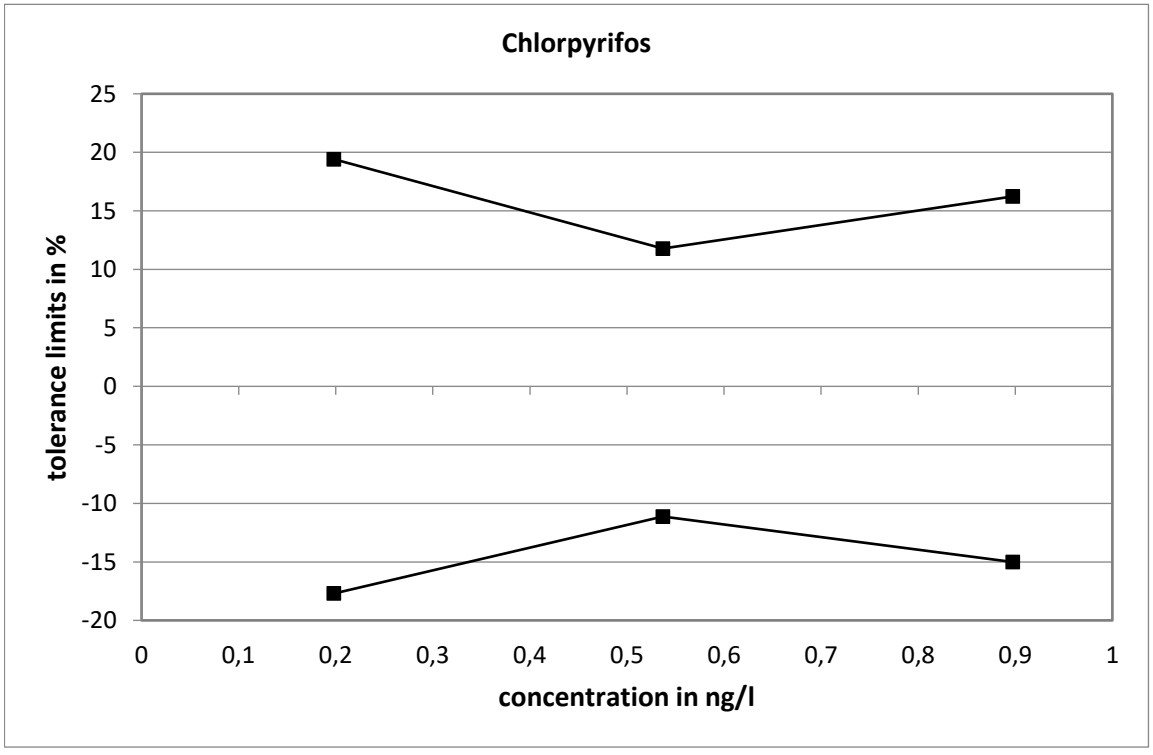
Recovery and matrix content



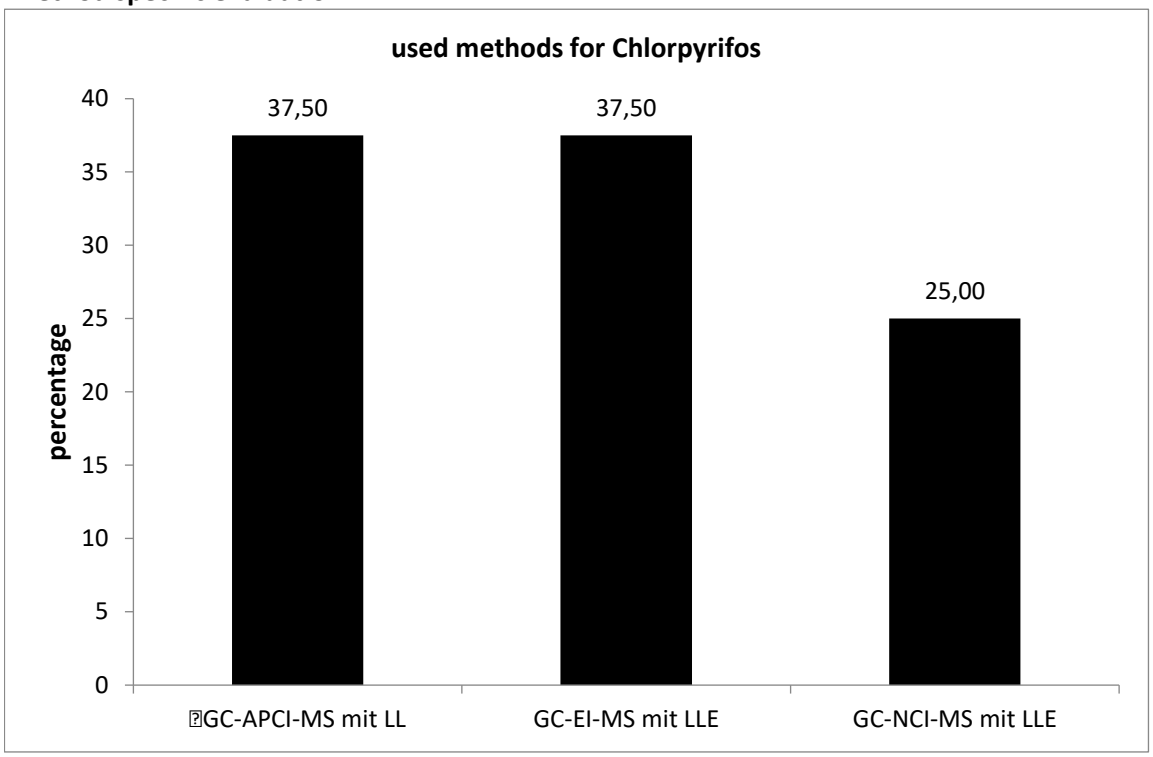
calculated matrix content: 0,028 ng/l average recovery: 97,6%

Relative standard deviation and tolerance limits





Method specific evaluation

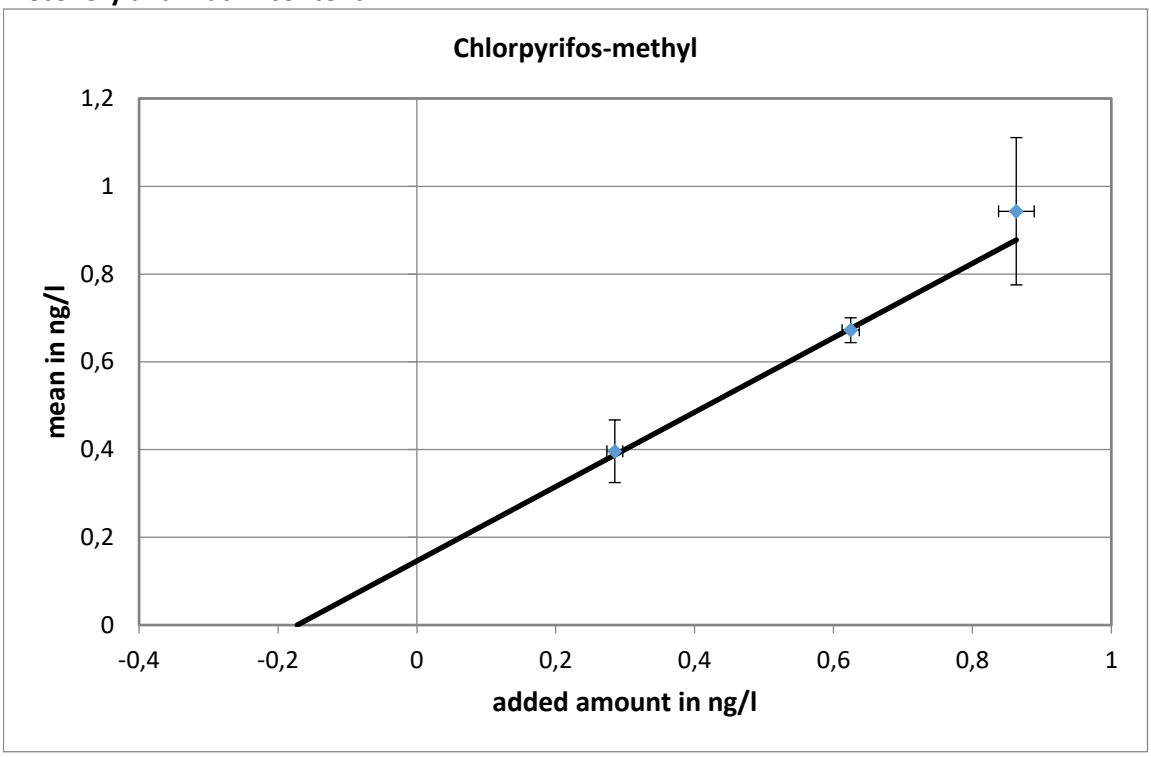


Due to the small number of participants, a comparison of methods is not meaningful.

Chlorpyrifos-methyl

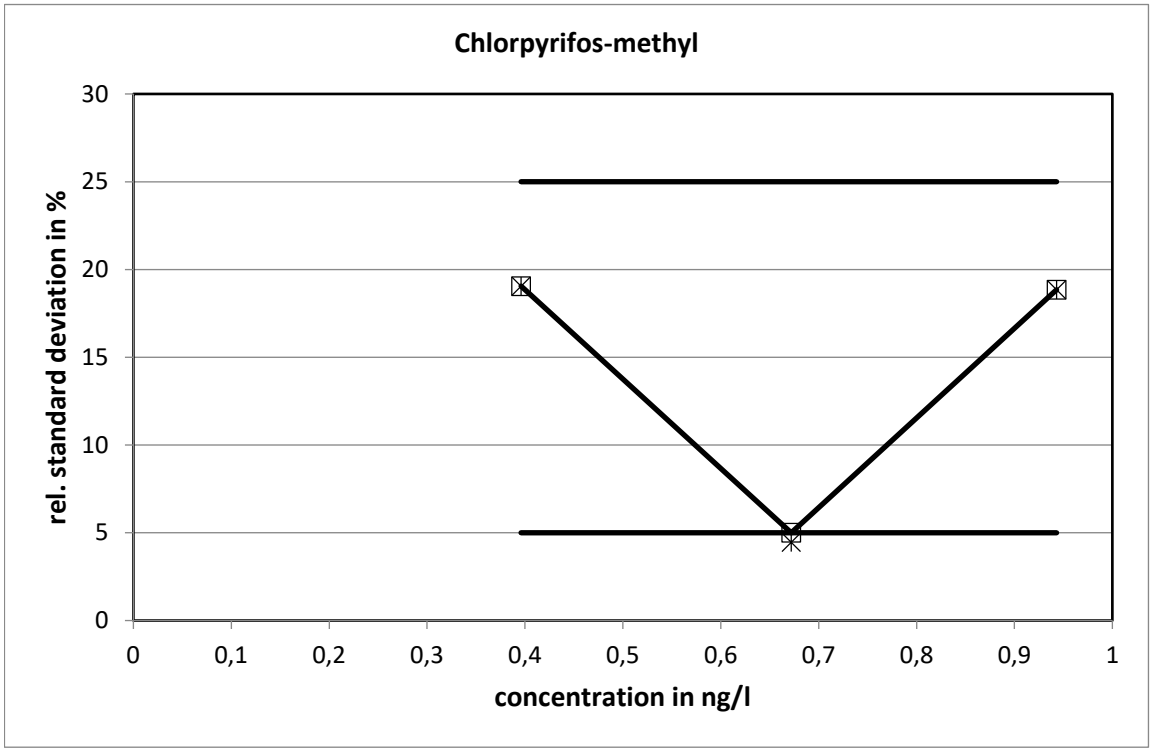
level	assigned value [ng/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [ng/l]	standard deviation for proficiency assessment [ng/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [ng/l]	lower tolerance limit [ng/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,3960	18,00	0,0755	0,0755	19,05	0,5642	0,2569	42,48	-35,13	7	0	1	12,5
2	0,6719	4,21	0,0300	0,0336	5,00	0,7409	0,6063	10,26	-9,76	7	1	3	50,0
3	0,9430	17,81	0,1777	0,1777	18,84	1,339	0,6151	41,95	-34,77	7	0	1	12,5
									sum	21	1	5	28,6

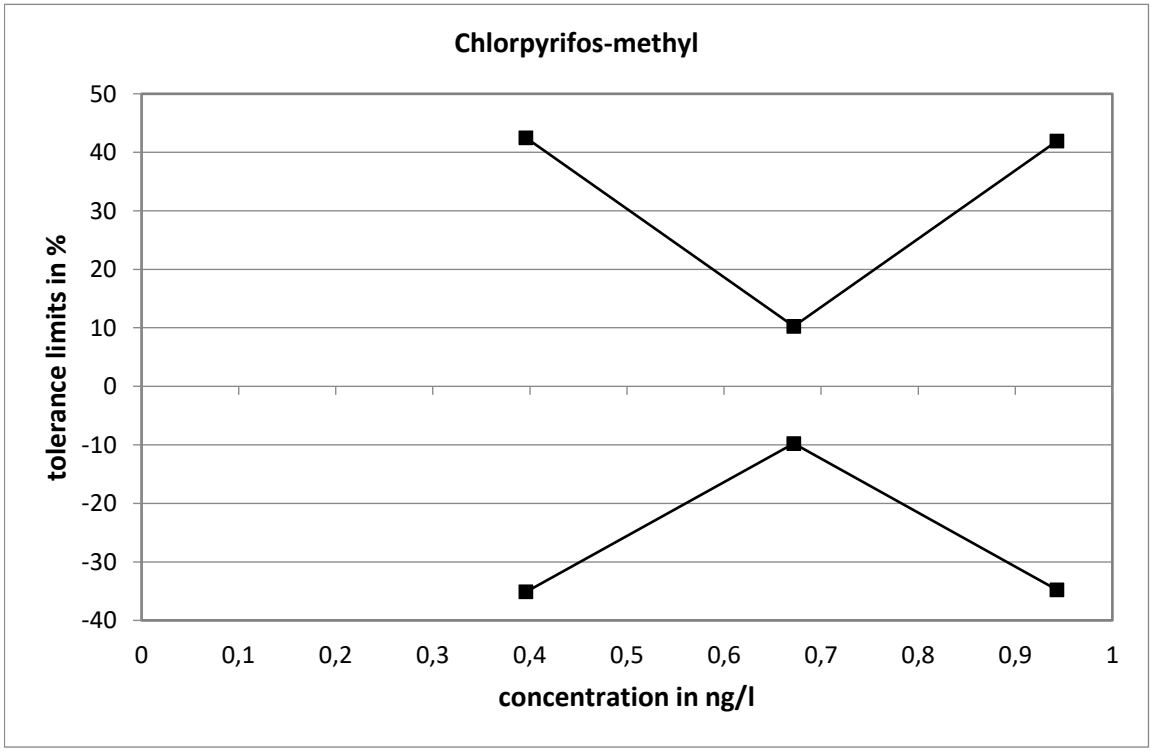
Recovery and matrix content



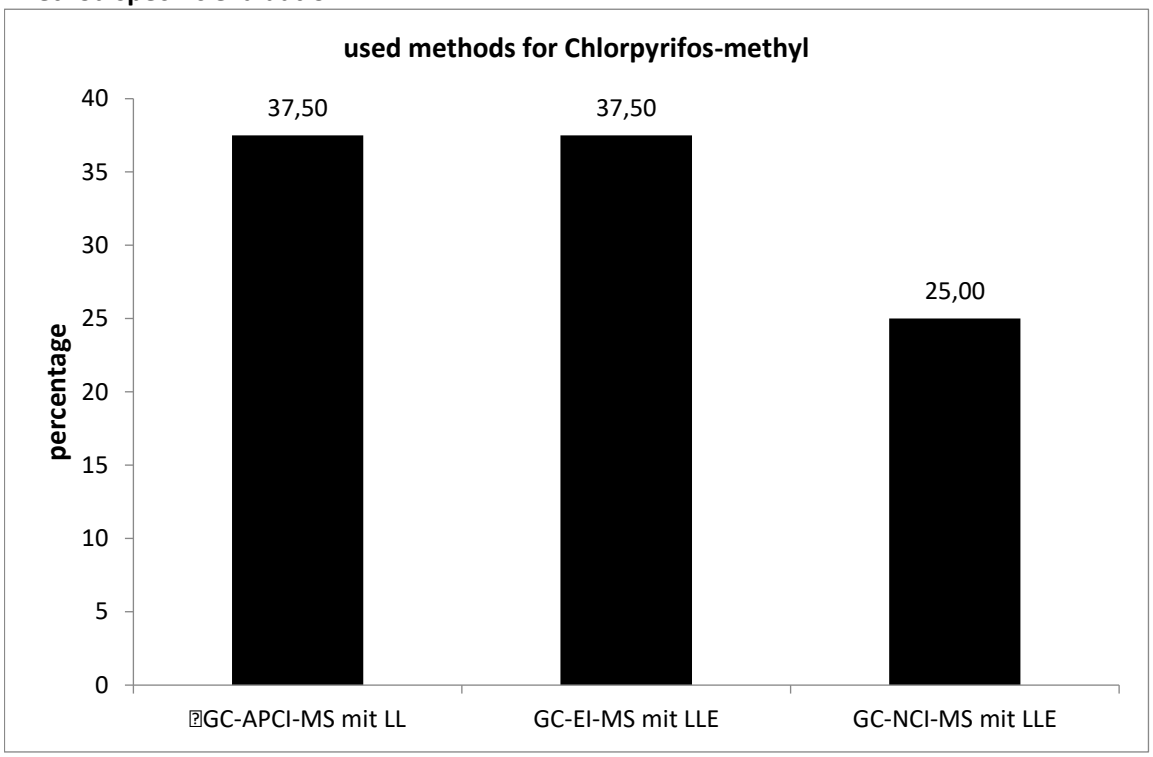
calculated matrix content: 0,173 ng/l average recovery: 84,8%

Relative standard deviation and tolerance limits





Method specific evaluation

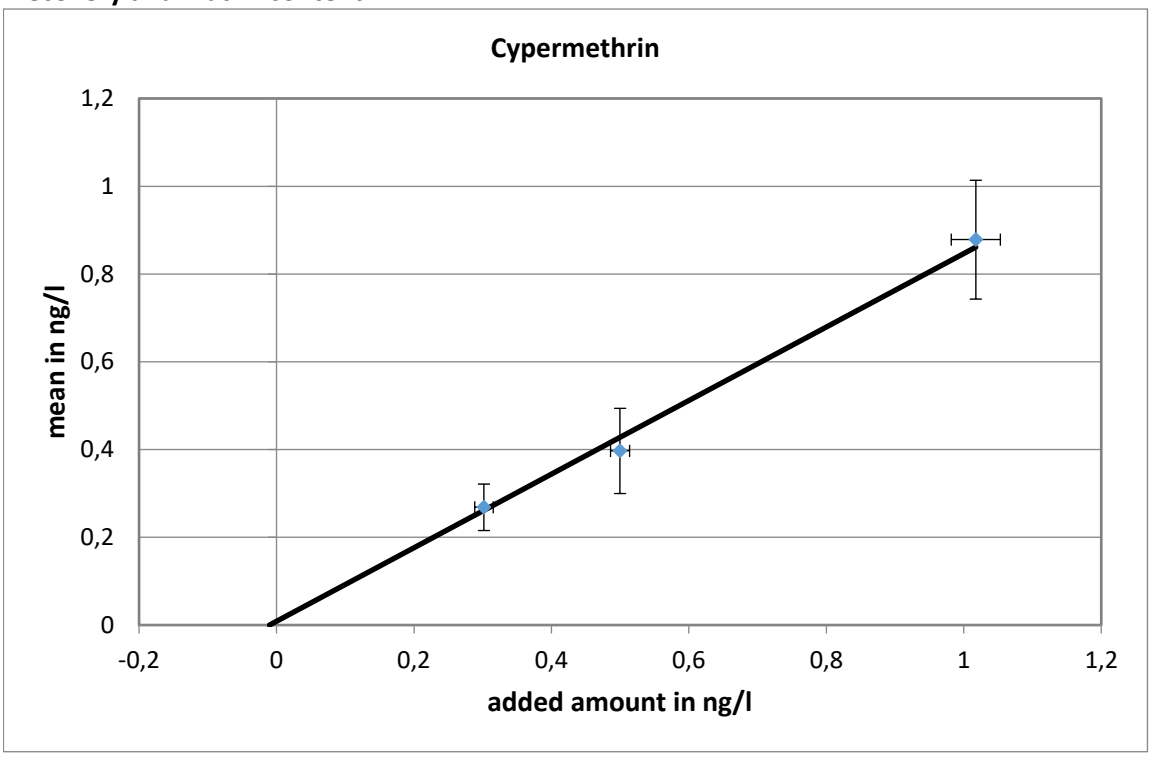


Due to the small number of participants, a comparison of methods is not meaningful.

Cypermethrin

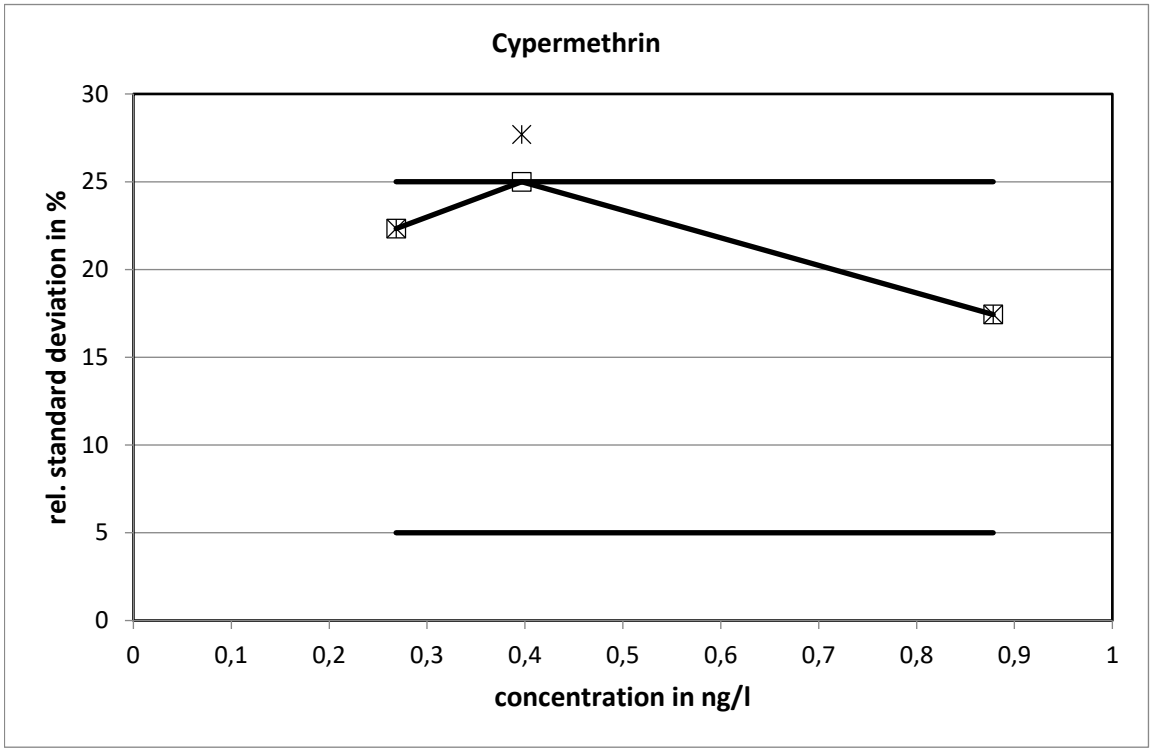
level	assigned value [ng/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [ng/l]	standard deviation for proficiency assessment [ng/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [ng/l]	lower tolerance limit [ng/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,2684	19,73	0,0599	0,0599	22,33	0,4048	0,1591	50,85	-40,71	8	0	1	11,1
2	0,3968	24,47	0,1098	0,0992	25,00	0,6269	0,2175	57,99	-45,19	8	1	1	22,2
3	0,8783	15,41	0,1531	0,1531	17,43	1,216	0,5943	38,47	-32,33	8	0	1	11,1
									sum	24	1	3	16,7

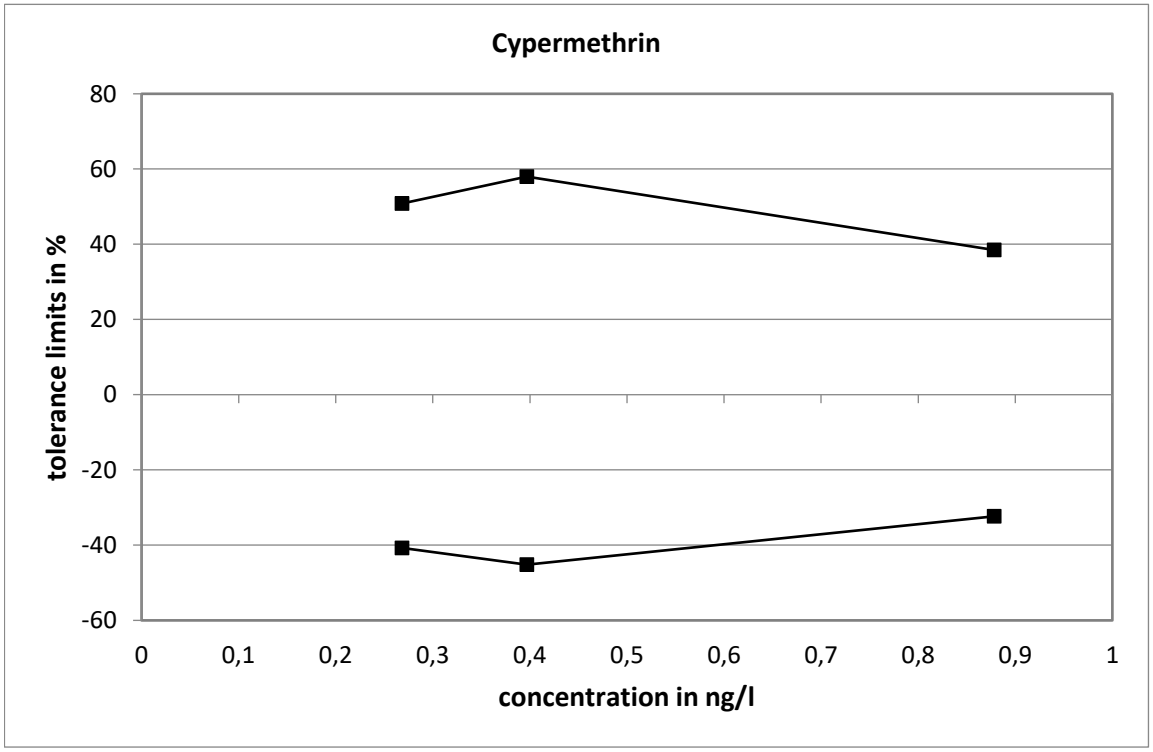
Recovery and matrix content



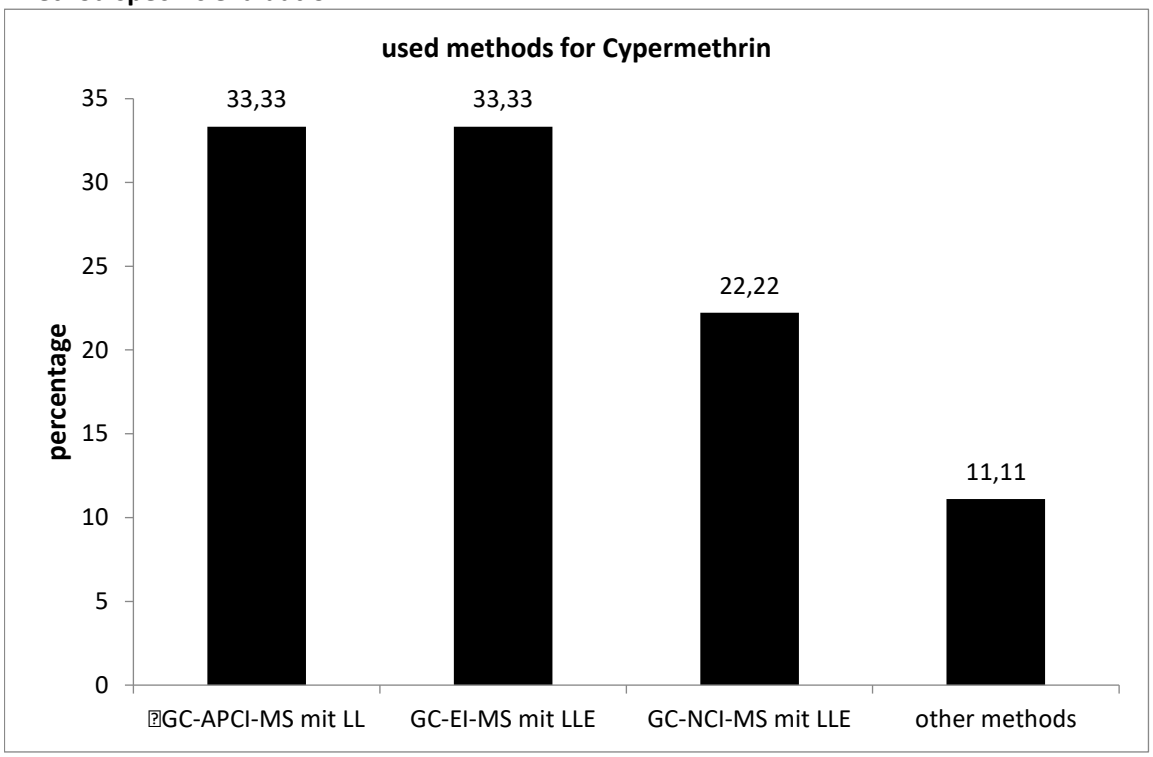
calculated matrix content: 0,01 ng/l average recovery: 83,8%

Relative standard deviation and tolerance limits





Method specific evaluation

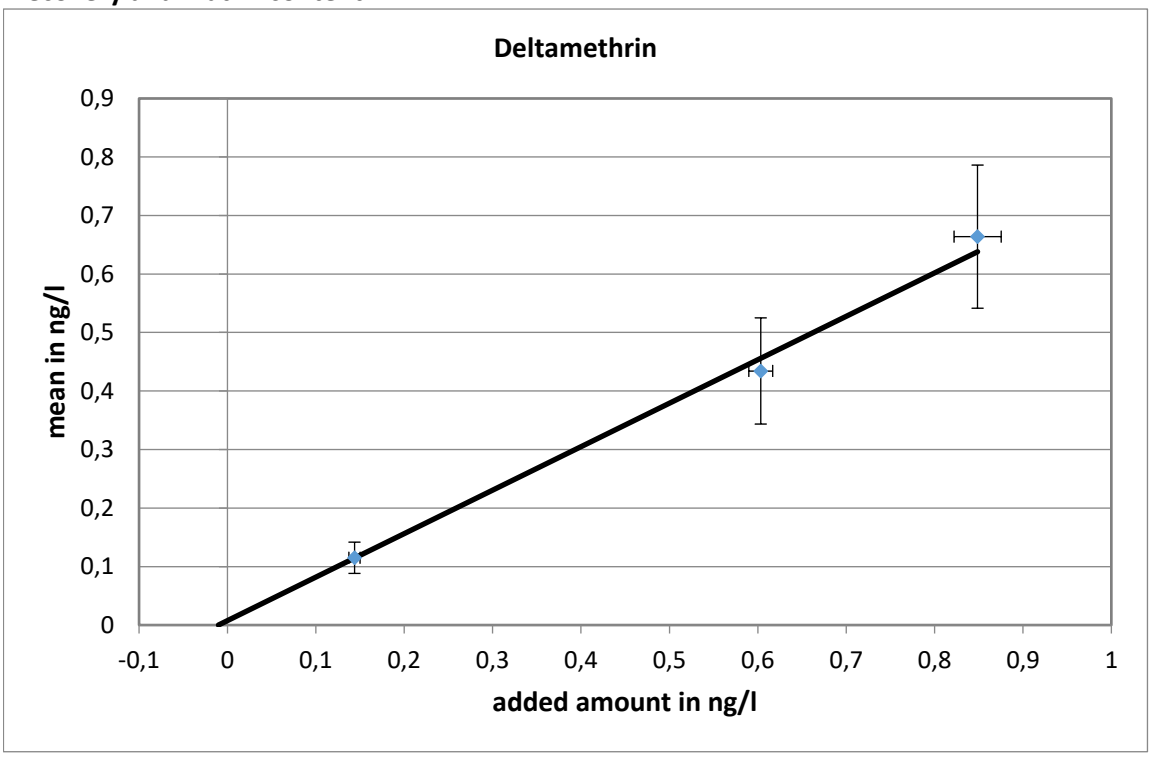


Due to the small number of participants, a comparison of methods is not meaningful.

Deltamethrin

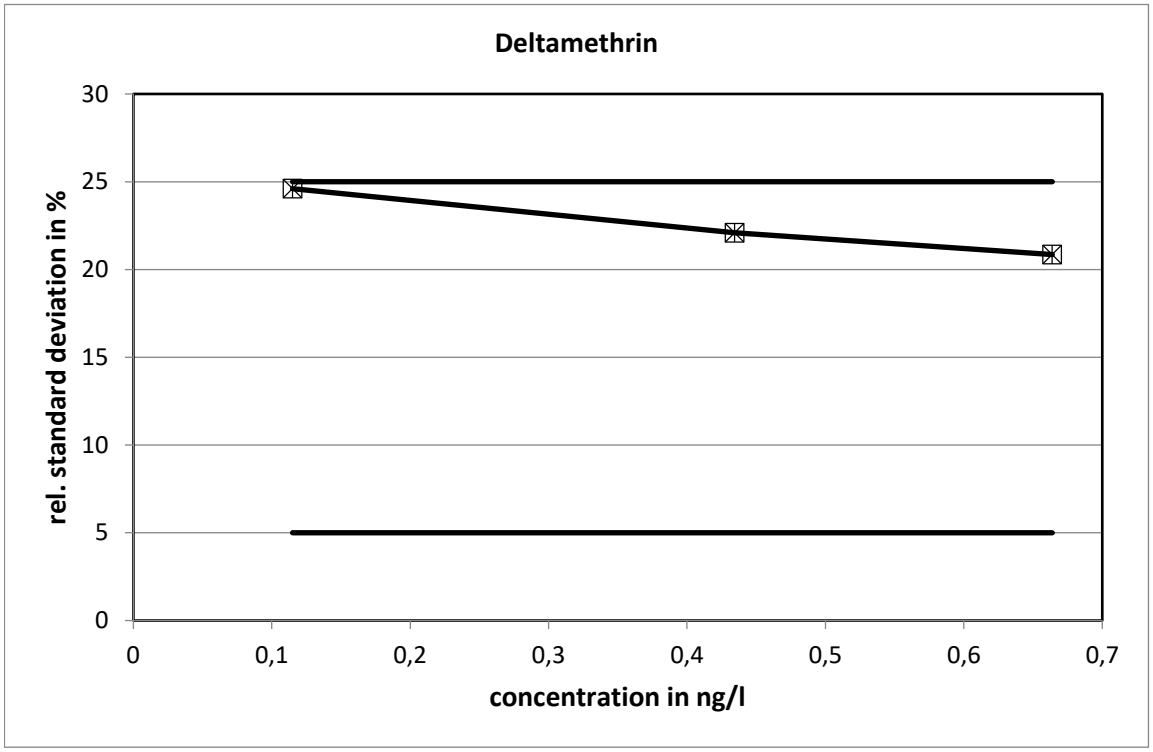
level	assigned value [ng/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [ng/l]	standard deviation for proficiency assessment [ng/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [ng/l]	lower tolerance limit [ng/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,1150	23,25	0,0283	0,0283	24,60	0,1804	0,0638	56,91	-44,53	7	0	2	22,2
2	0,4343	20,88	0,0960	0,0960	22,10	0,6526	0,2592	50,26	-40,32	7	1	1	22,2
3	0,6639	18,43	0,1384	0,1384	20,85	0,9761	0,4102	47,03	-38,21	8	0	1	11,1
									sum	22	1	4	22,7

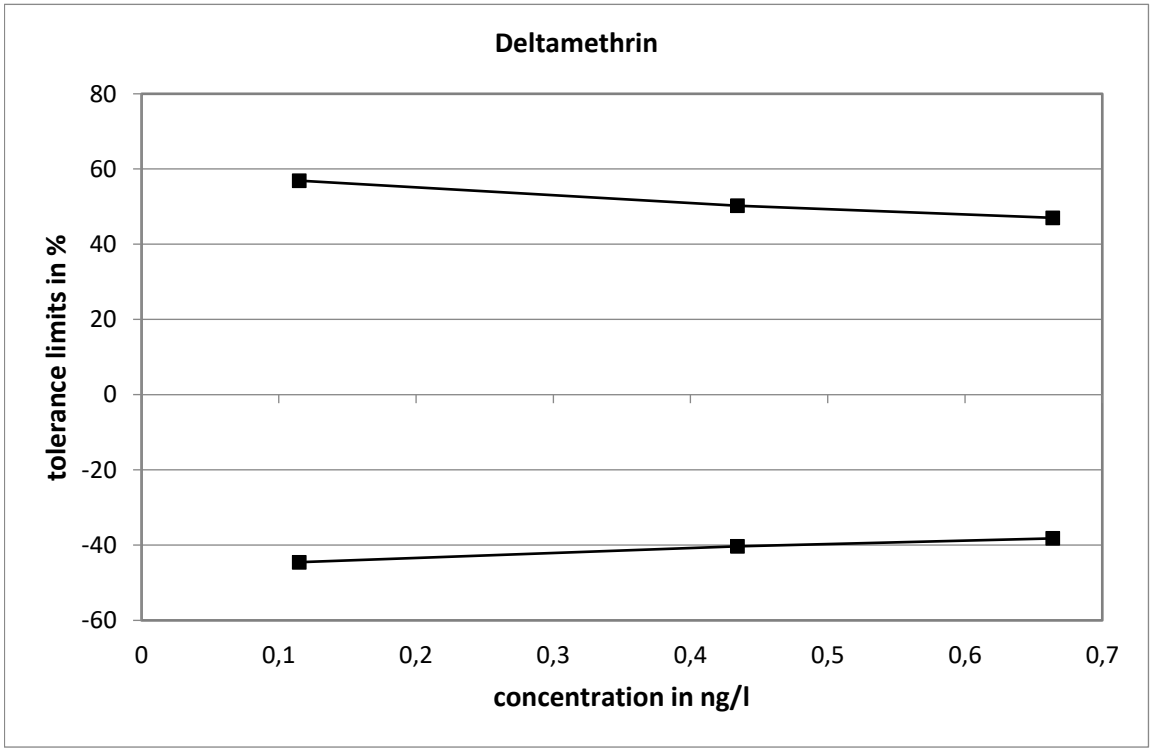
Recovery and matrix content



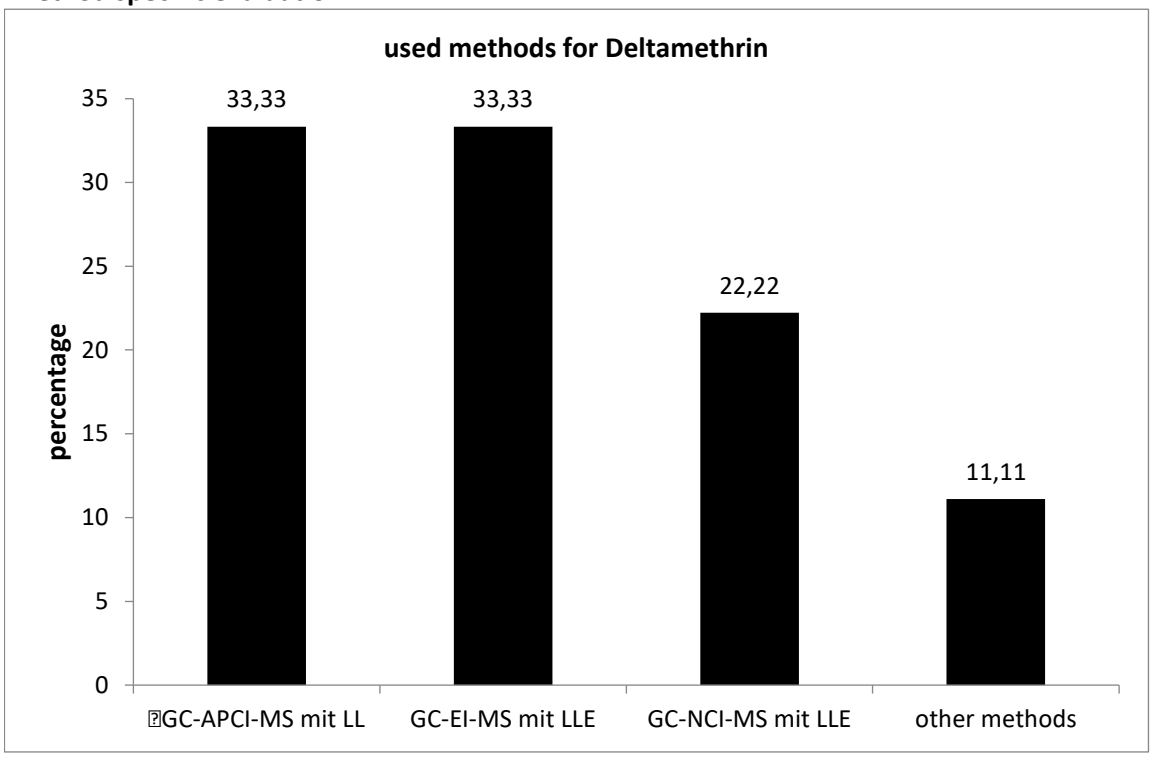
calculated matrix content: 0,01 ng/l average recovery: 74,3%

Relative standard deviation and tolerance limits





Method specific evaluation

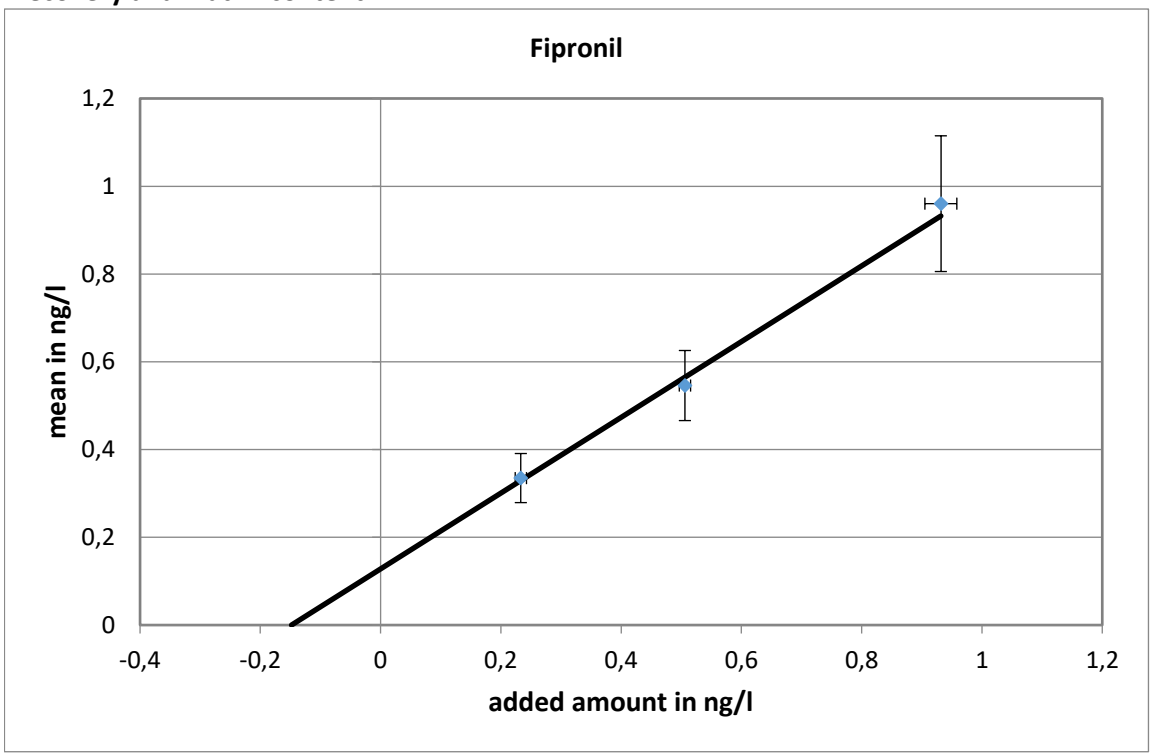


Due to the small number of participants, a comparison of methods is not meaningful.

Fipronil

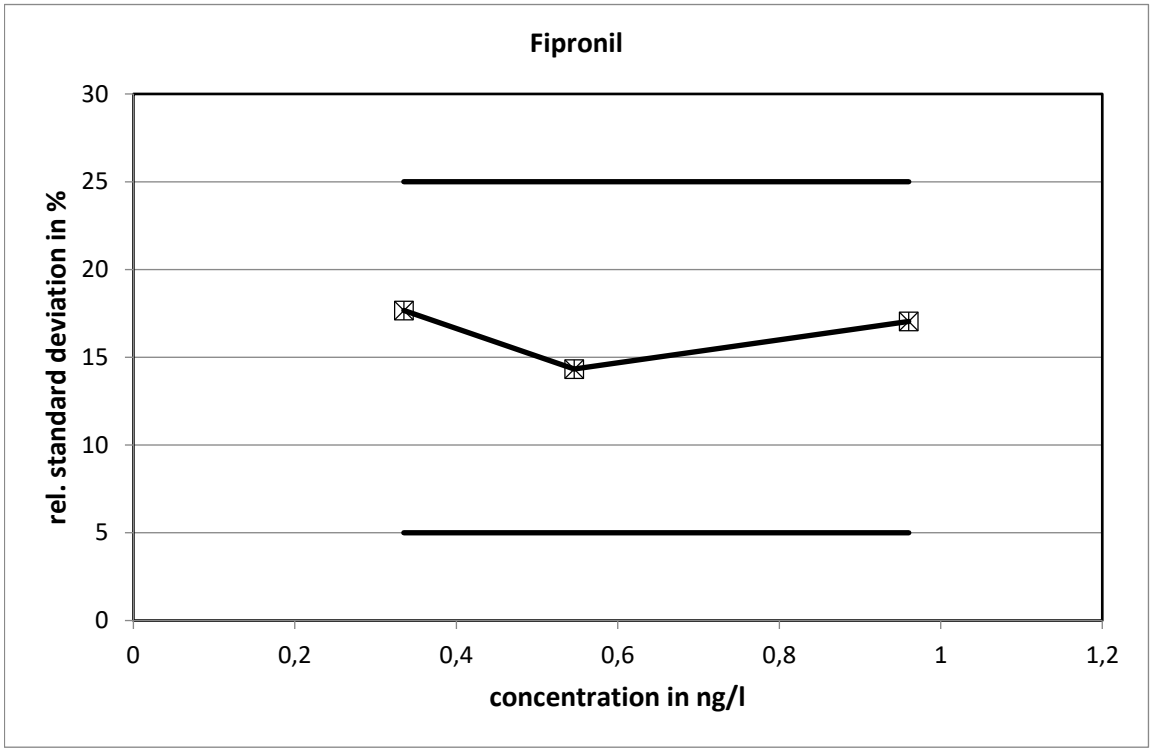
level	assigned value [ng/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [ng/l]	standard deviation for proficiency assessment [ng/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [ng/l]	lower tolerance limit [ng/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,3350	16,69	0,0592	0,0592	17,67	0,4657	0,2253	39,04	-32,74	7	0	0	0,0
2	0,5458	14,63	0,0782	0,0782	14,33	0,7152	0,3990	31,02	-26,89	6	1	0	14,3
3	0,9603	16,10	0,1637	0,1637	17,04	1,321	0,6563	37,51	-31,65	7	0	0	0,0
									sum	20	1	0	5,0

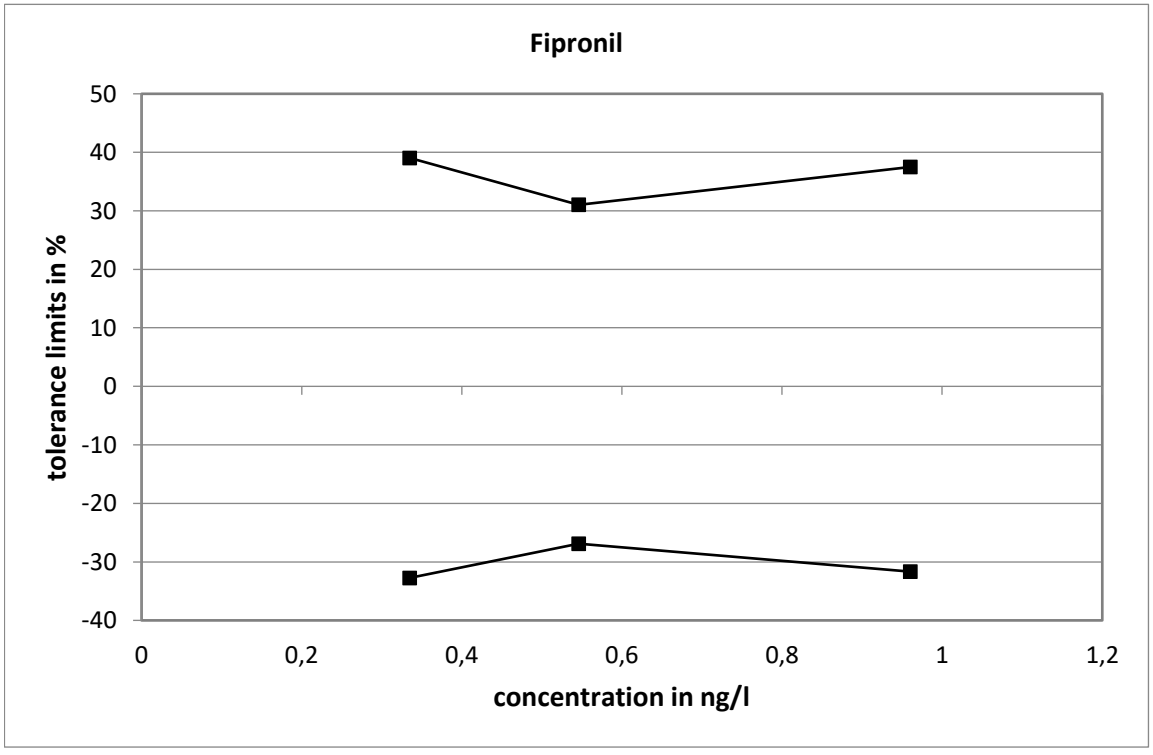
Recovery and matrix content



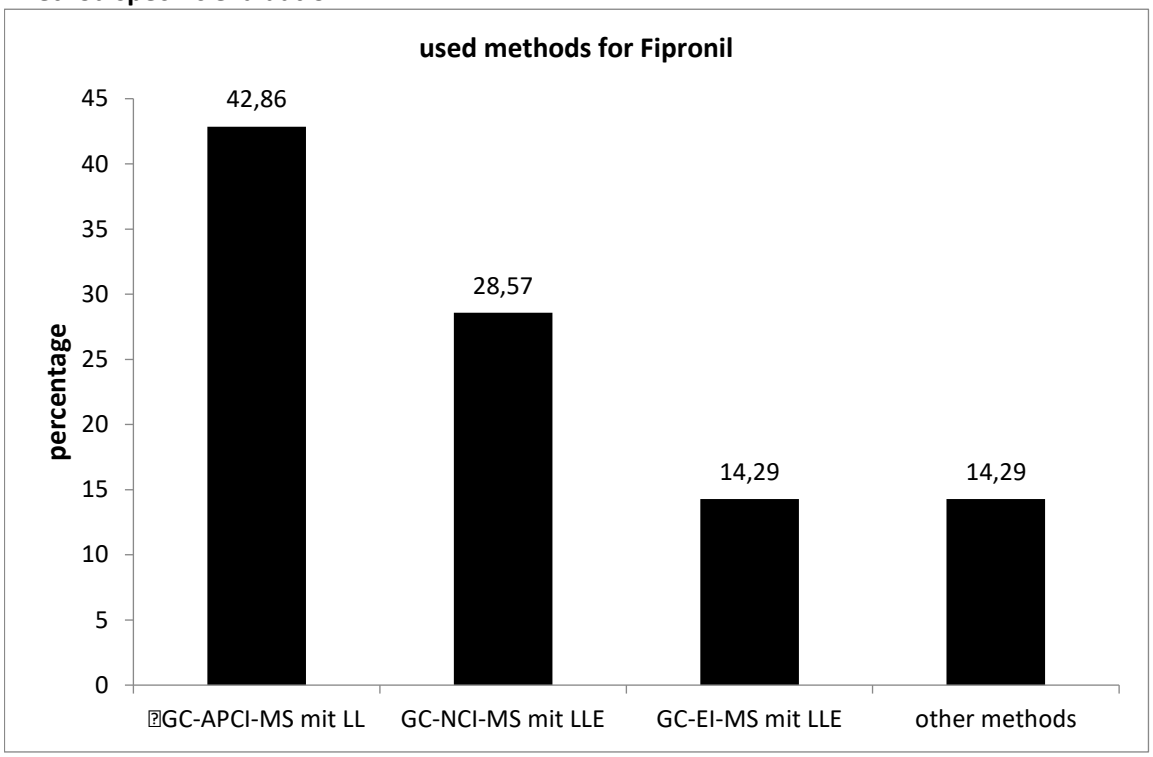
calculated matrix content: 0,148 ng/l average recovery: 86,3%

Relative standard deviation and tolerance limits





Method specific evaluation

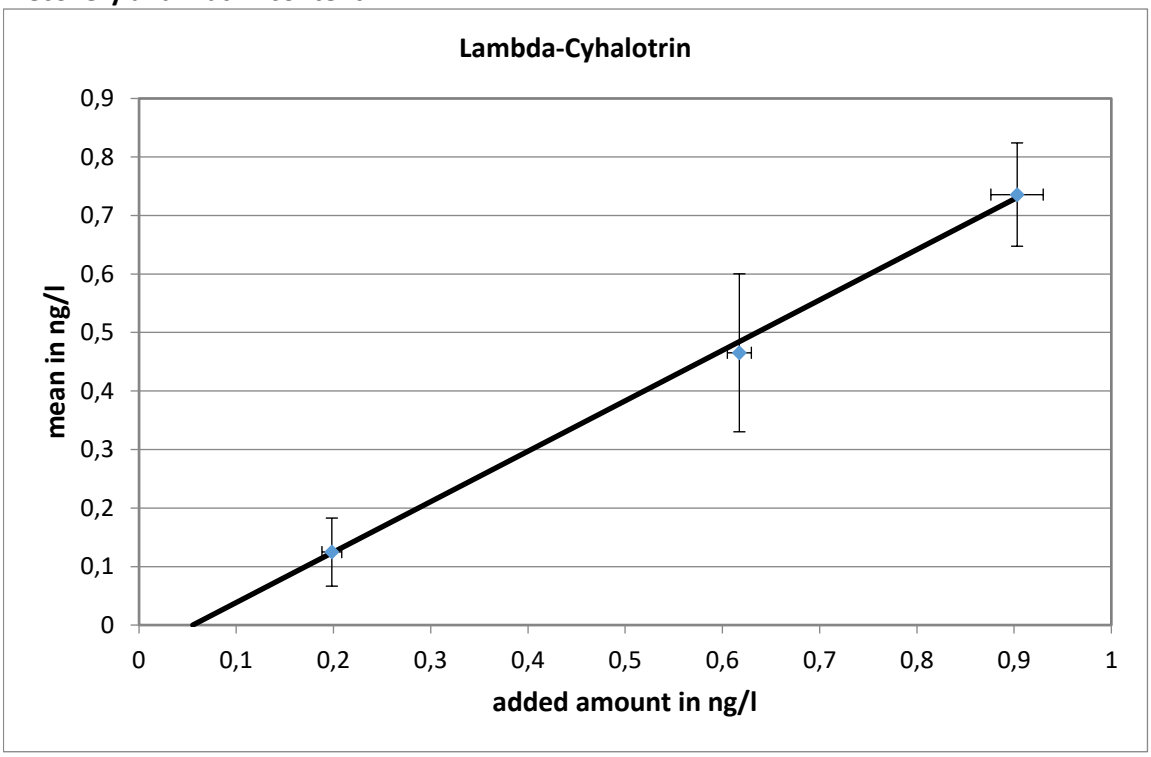


Due to the small number of participants, a comparison of methods is not meaningful.

Lambda-Cyhalotrin

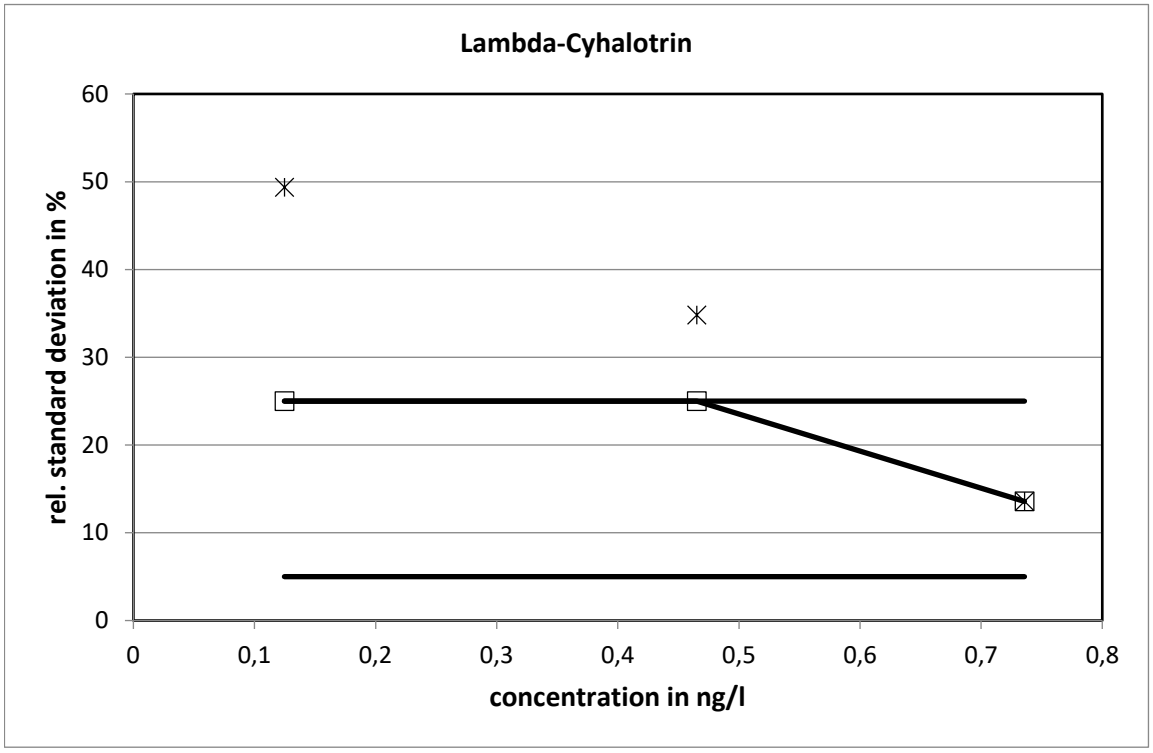
level	assigned value [ng/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [ng/l]	standard deviation for proficiency assessment [ng/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [ng/l]	lower tolerance limit [ng/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,1247	46,66	0,0616	0,0312	25,00	0,1970	0,0684	57,99	-45,19	7	1	3	44,4
2	0,4653	29,01	0,1620	0,1163	25,00	0,7351	0,2550	57,99	-45,19	9	1	1	22,2
3	0,7358	12,00	0,0999	0,0999	13,57	0,9509	0,5478	29,25	-25,54	8	0	1	11,1
									sum	24	2	5	29,2

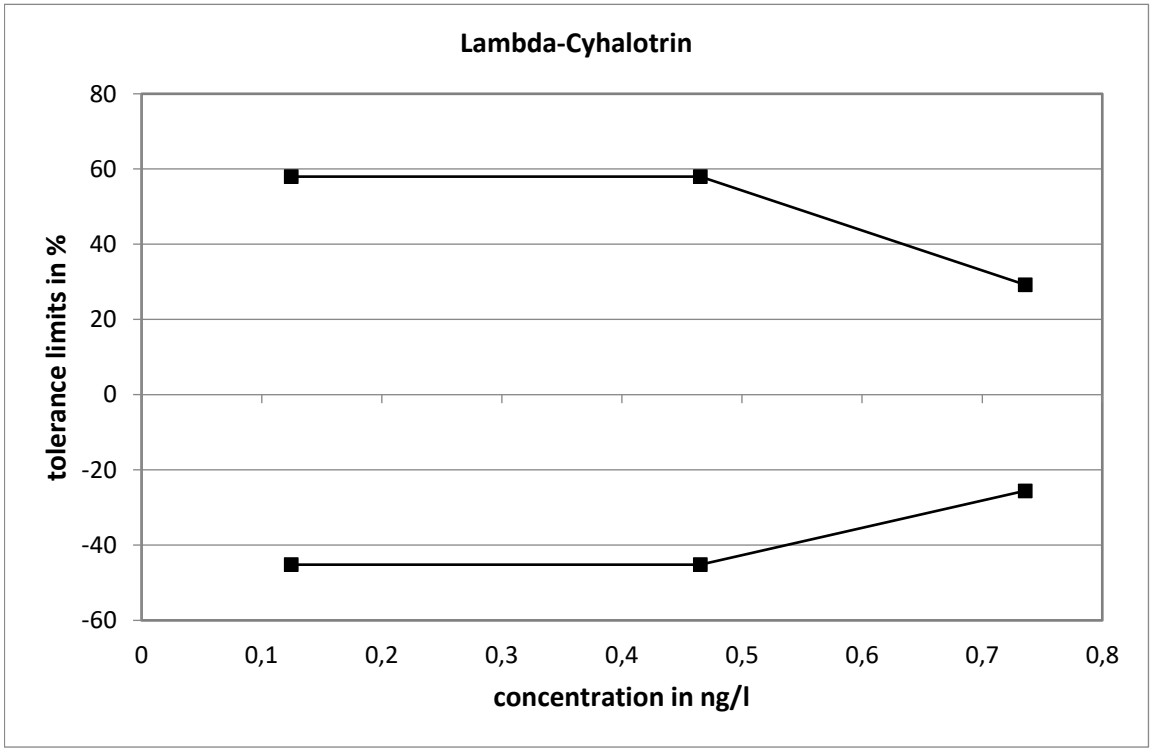
Recovery and matrix content



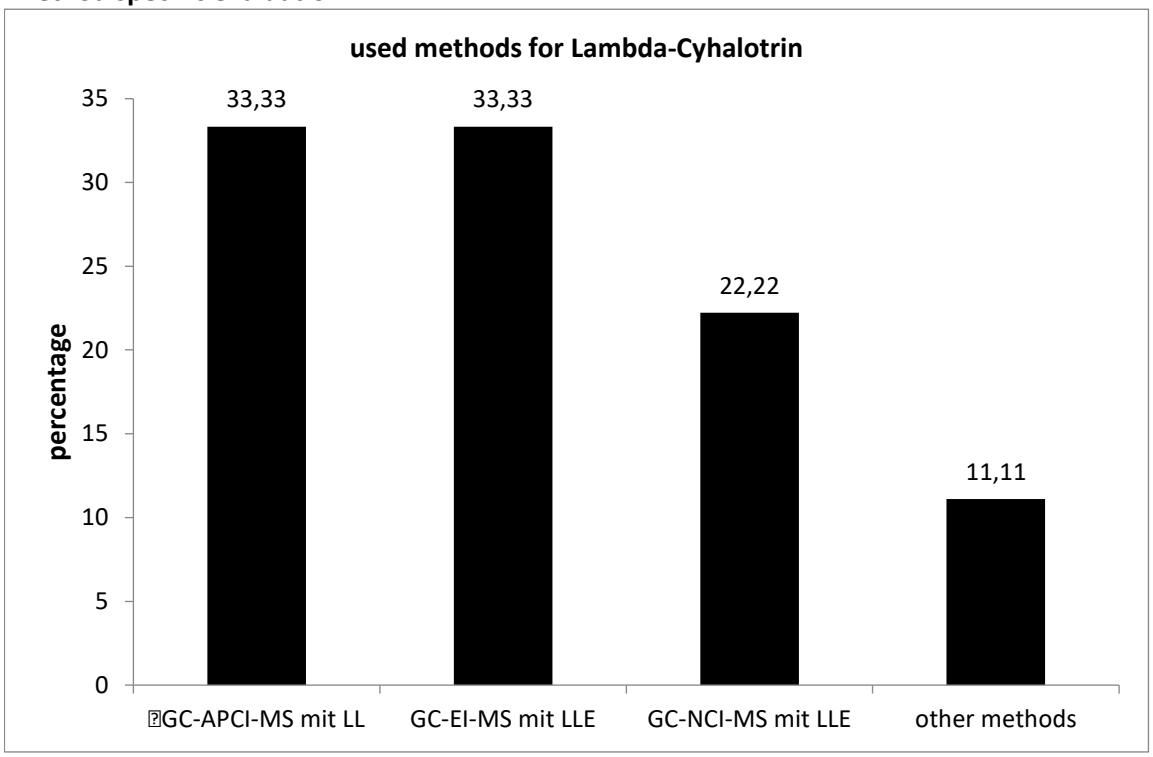
calculated matrix content: 0 ng/l average recovery: 86,2%

Relative standard deviation and tolerance limits





Method specific evaluation

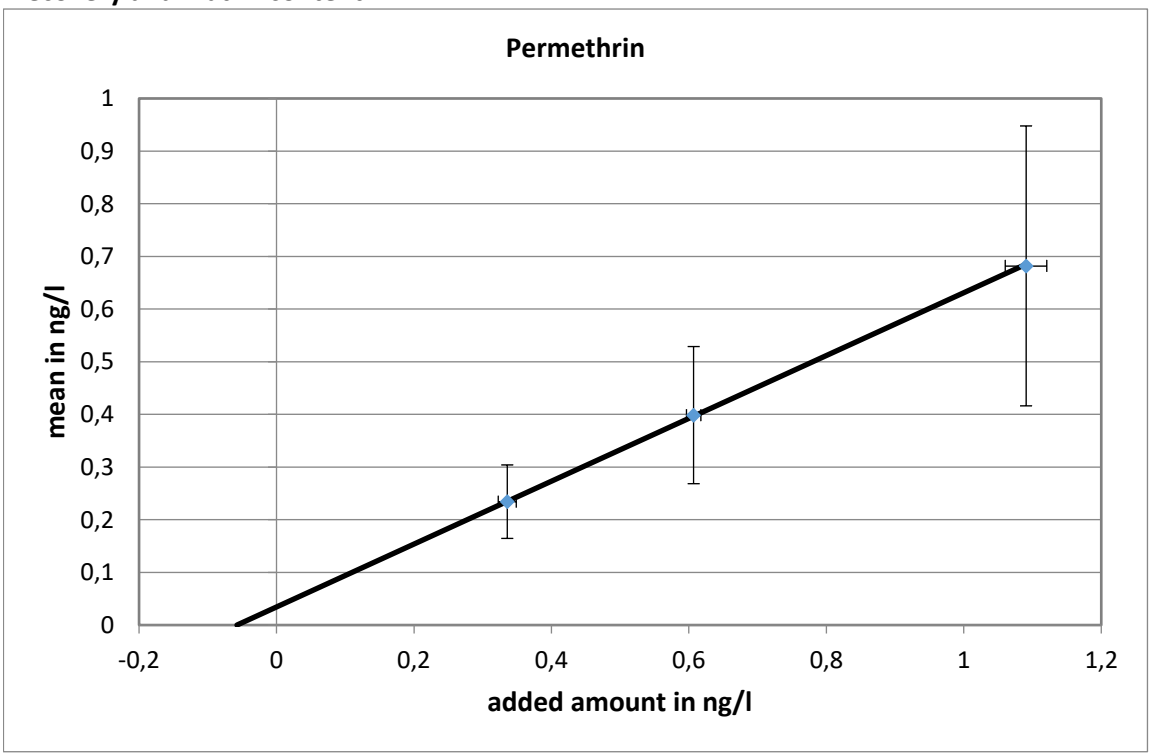


Due to the small number of participants, a comparison of methods is not meaningful.

Permethrin

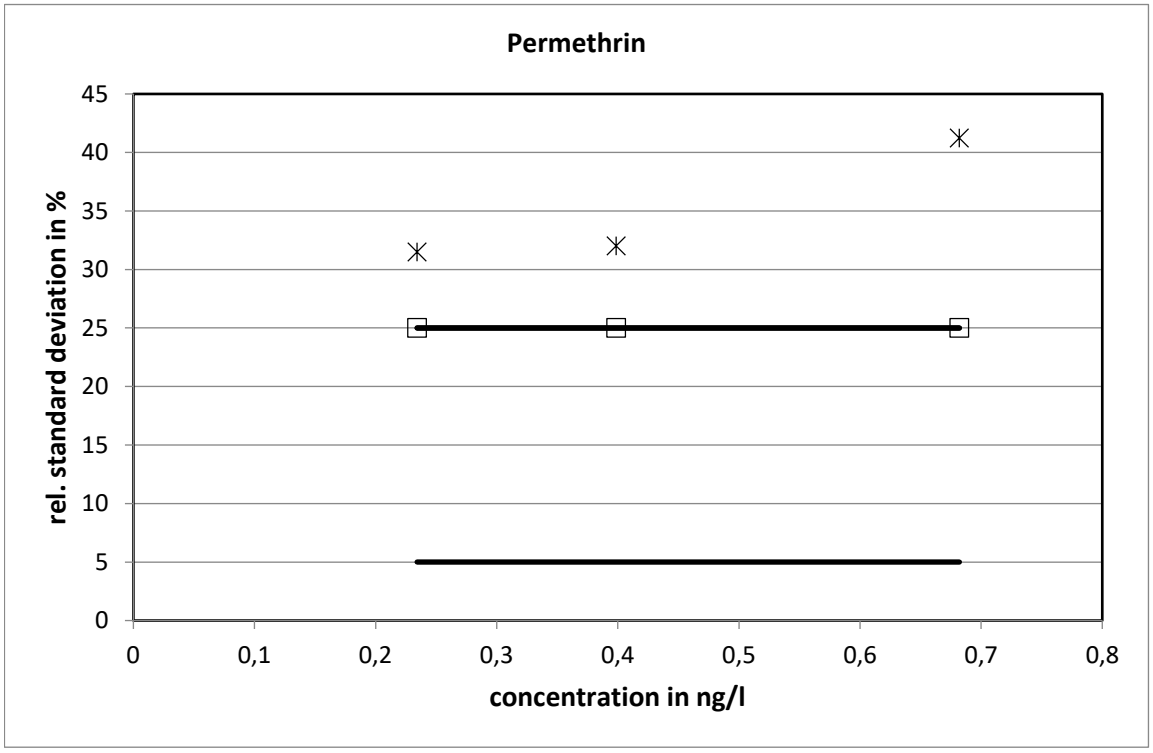
level	assigned value [ng/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [ng/l]	standard deviation for proficiency assessment [ng/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [ng/l]	lower tolerance limit [ng/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,2343	29,76	0,0738	0,0586	25,00	0,3701	0,1284	57,99	-45,19	7	0	1	12,5
2	0,3987	32,67	0,1276	0,0997	25,00	0,6298	0,2185	57,99	-45,19	6	1	1	25,0
3	0,6820	38,97	0,2813	0,1705	25,00	1,077	0,3738	57,99	-45,19	7	0	1	12,5
									sum	20	1	3	20,0

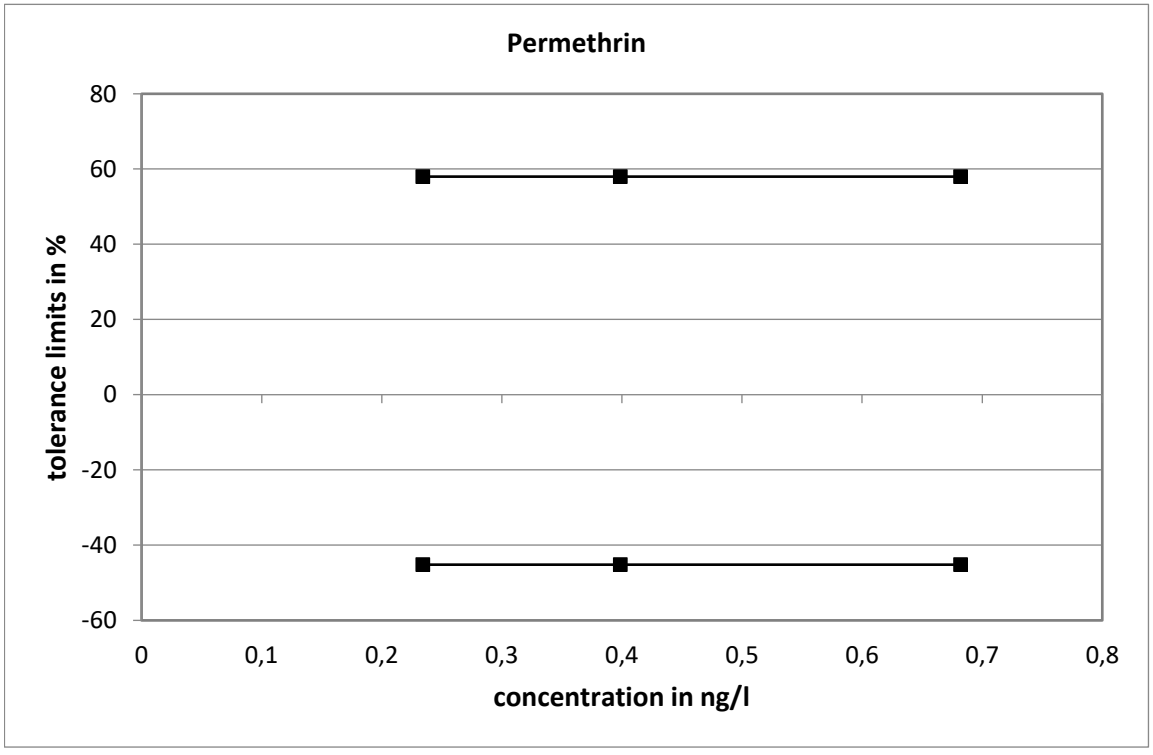
Recovery and matrix content



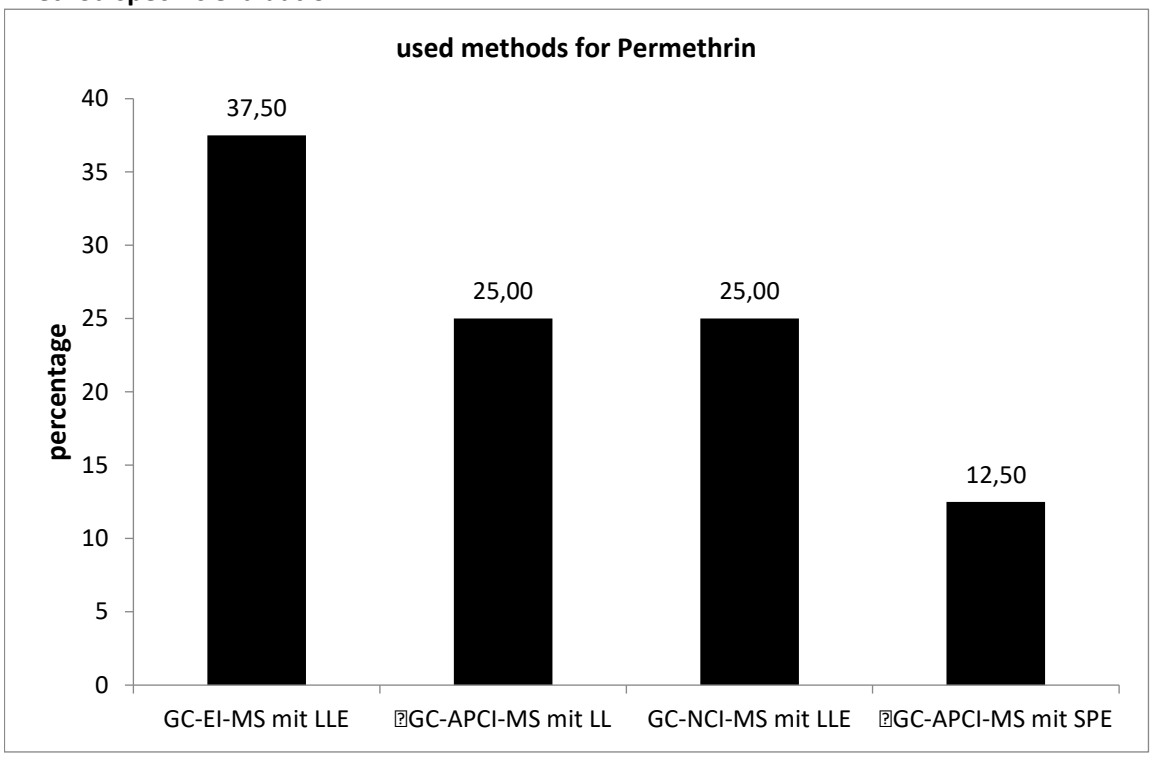
calculated matrix content: 0,058 ng/l average recovery: 59,7%

Relative standard deviation and tolerance limits





Method specific evaluation

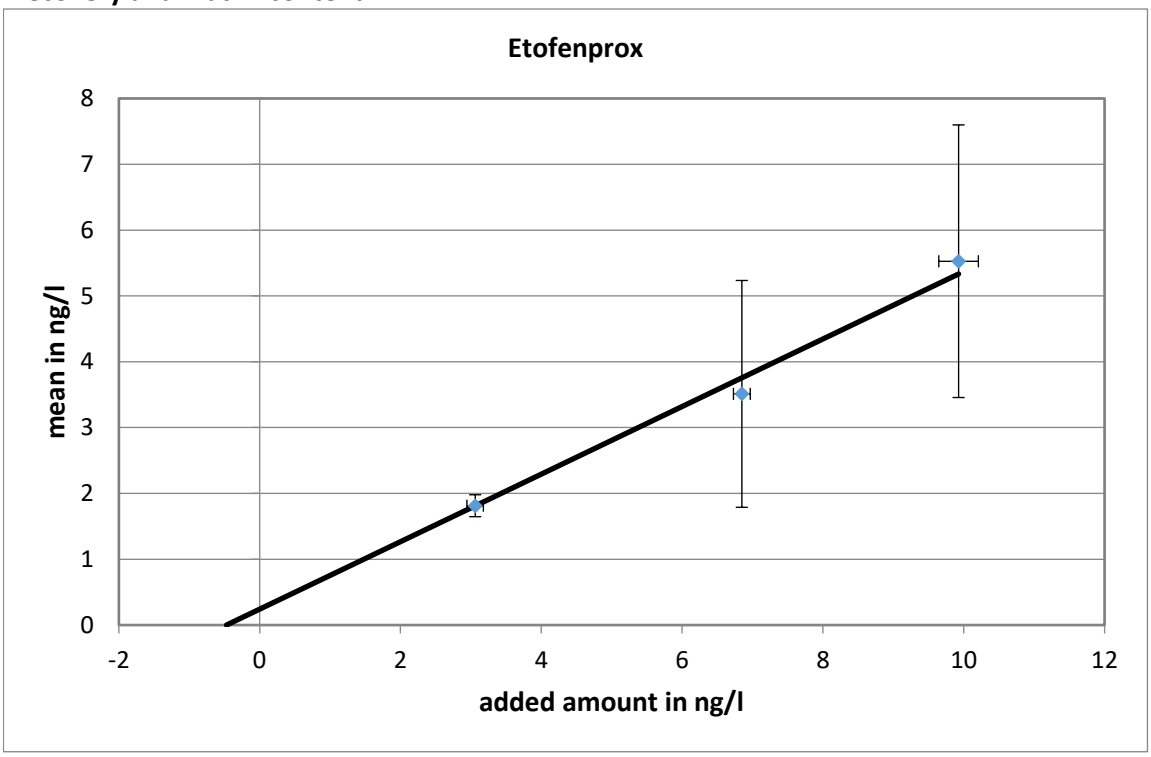


Due to the small number of participants, a comparison of methods is not meaningful.

Etofenprox

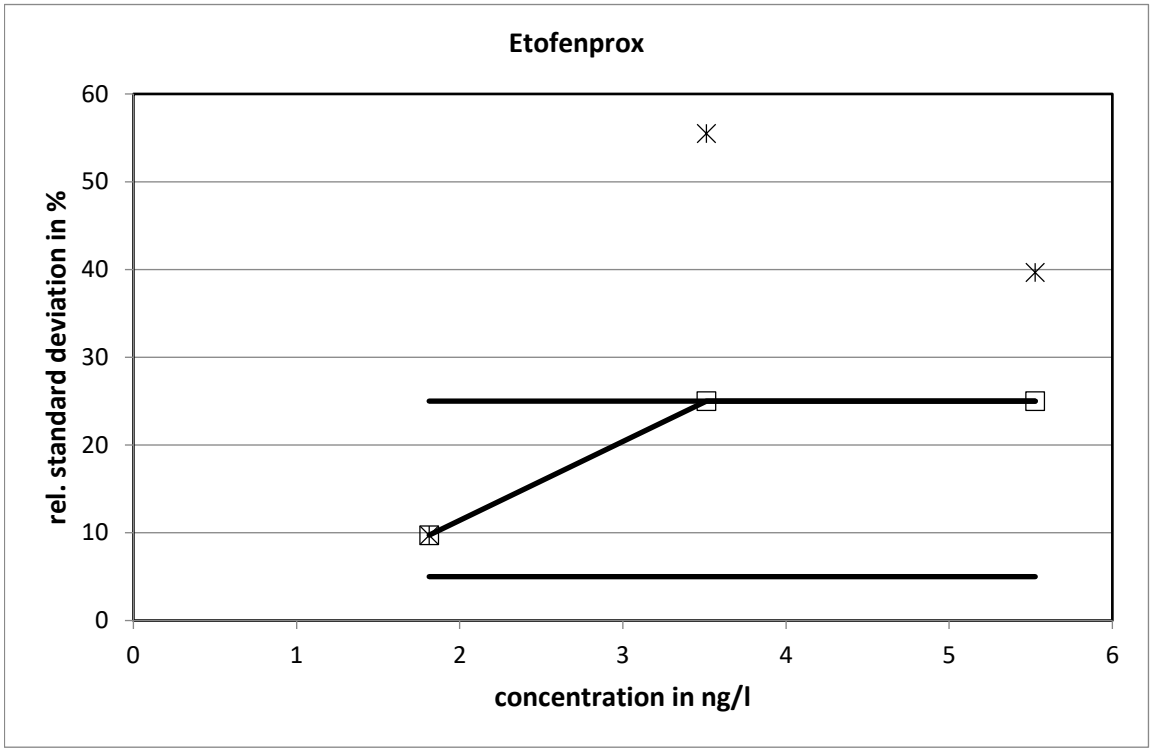
level	assigned value [ng/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [ng/l]	standard deviation for proficiency assessment [ng/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [ng/l]	lower tolerance limit [ng/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	1,813	9,20	0,1764	0,1764	9,73	2,185	1,476	20,50	-18,61	7	0	2	25,0
2	3,512	49,06	1,950	0,8780	25,00	5,548	1,925	57,99	-45,19	8	1	0	12,5
3	5,527	37,46	2,191	1,382	25,00	8,732	3,030	57,99	-45,19	7	0	1	12,5
									sum	22	1	3	18,2

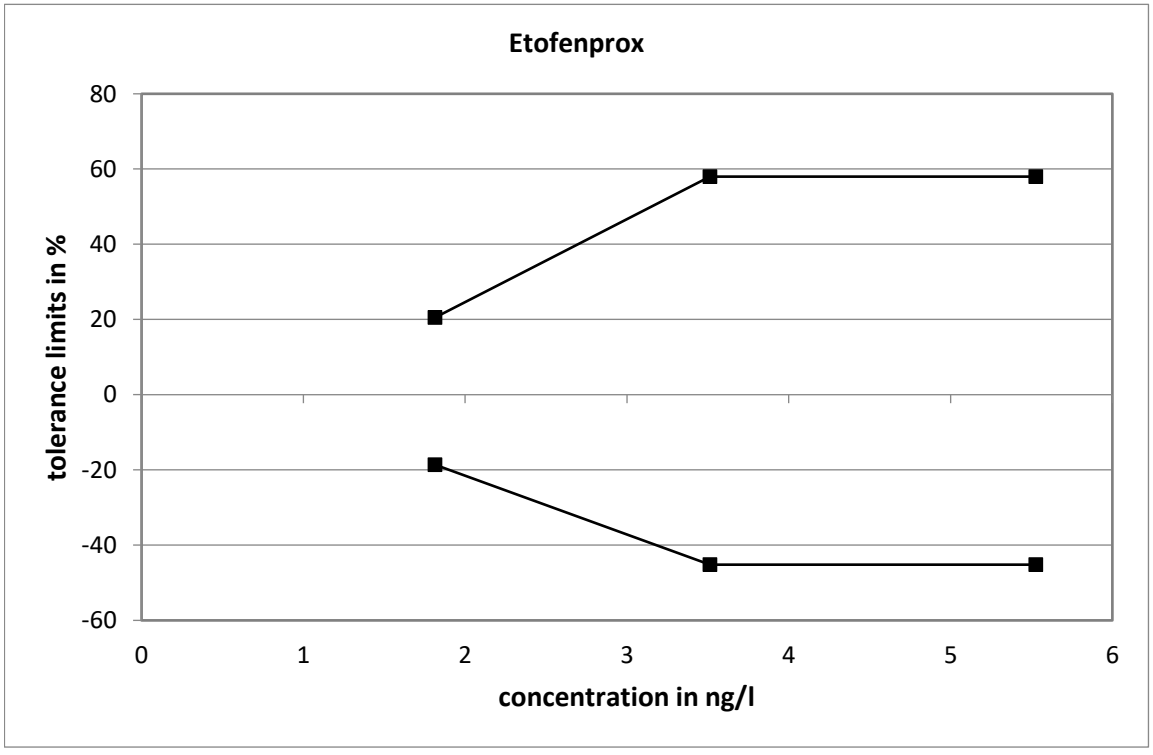
Recovery and matrix content



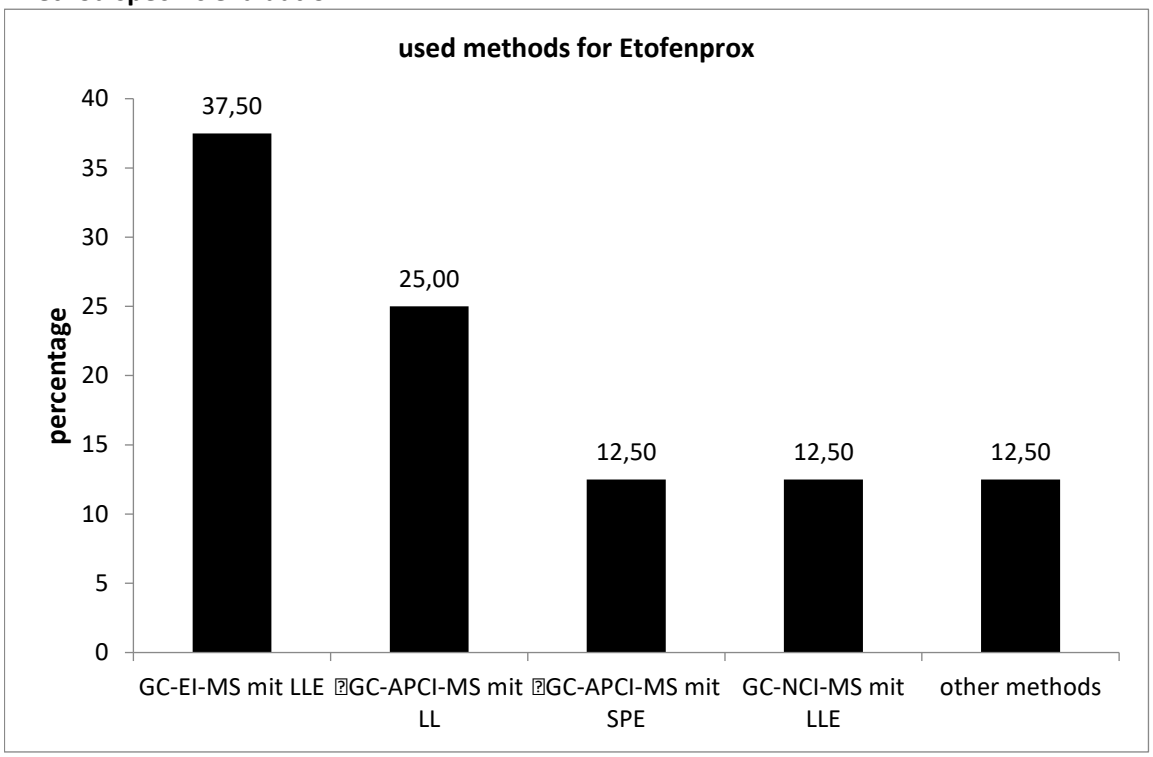
calculated matrix content 0,472 ng/l average recovery: 51,3%

Relative standard deviation and tolerance limits





Method specific evaluation

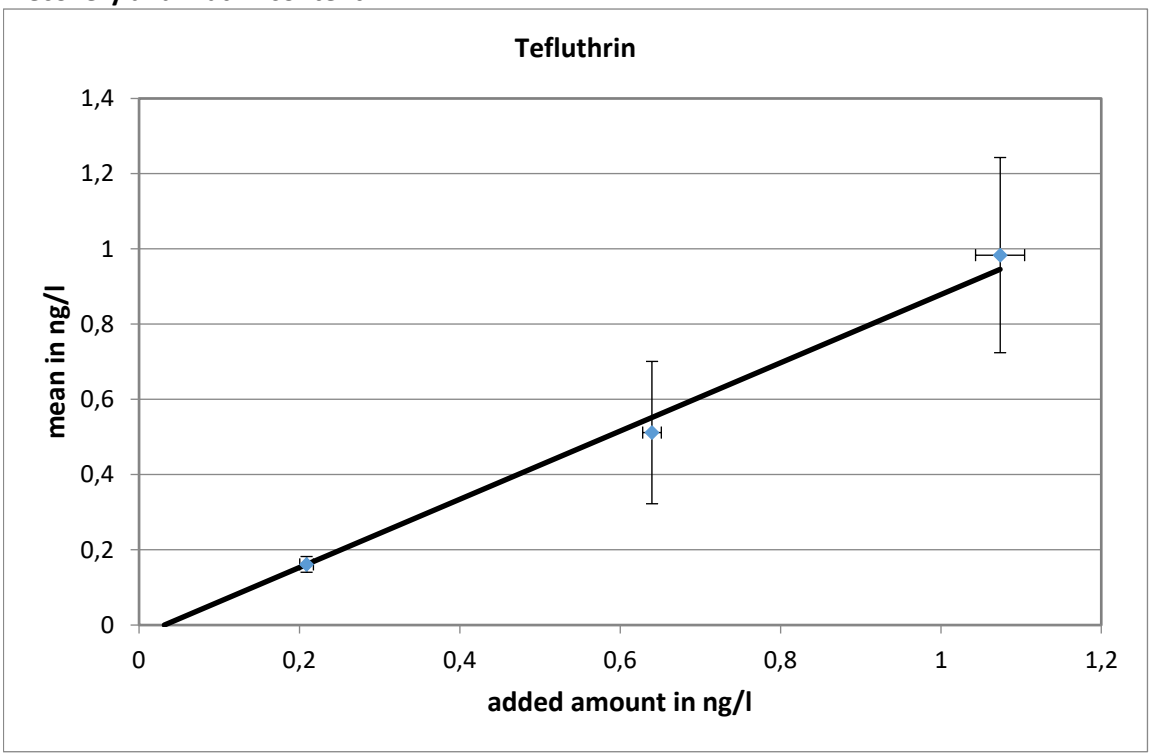


Due to the small number of participants, a comparison of methods is not meaningful.

Tefluthrin

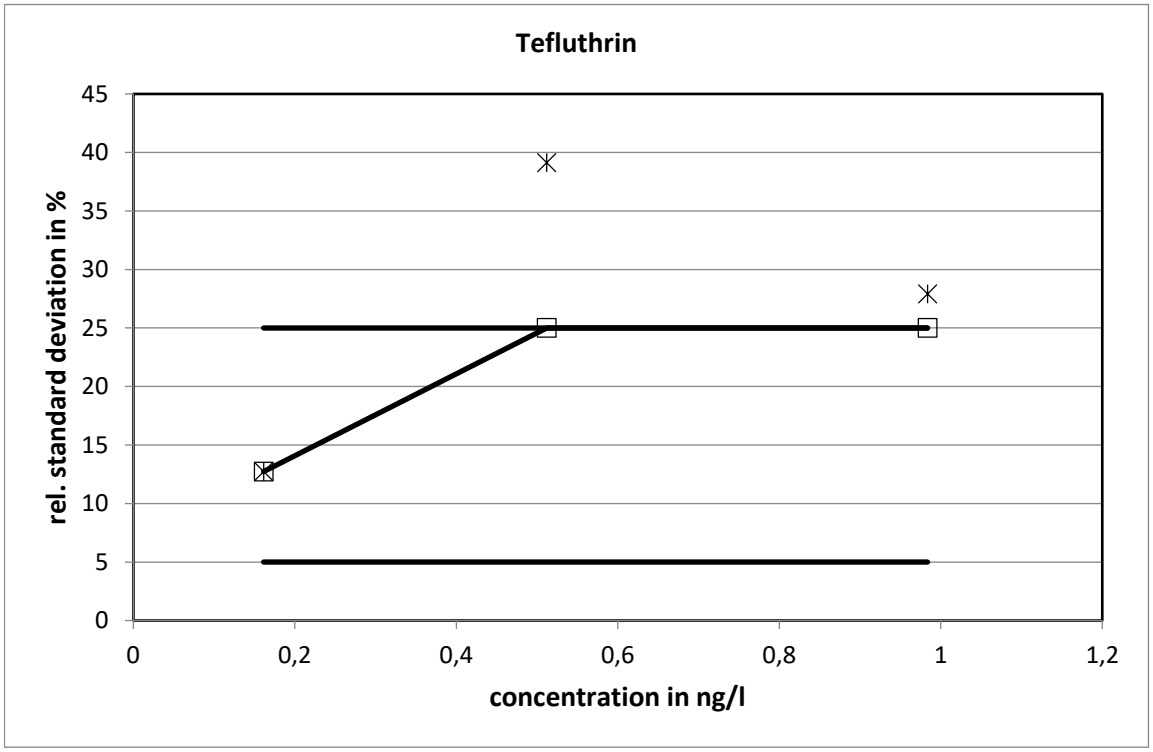
level	assigned value [ng/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [ng/l]	standard deviation for proficiency assessment [ng/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [ng/l]	lower tolerance limit [ng/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,1613	12,99	0,0205	0,0205	12,73	0,2053	0,1225	27,29	-24,04	6	1	1	28,6
2	0,5117	36,98	0,2003	0,1279	25,00	0,8084	0,2805	57,99	-45,19	7	0	0	0,0
3	0,9836	26,38	0,2746	0,2459	25,00	1,554	0,5391	57,99	-45,19	7	1	0	14,3
									sum	20	2	1	15,0

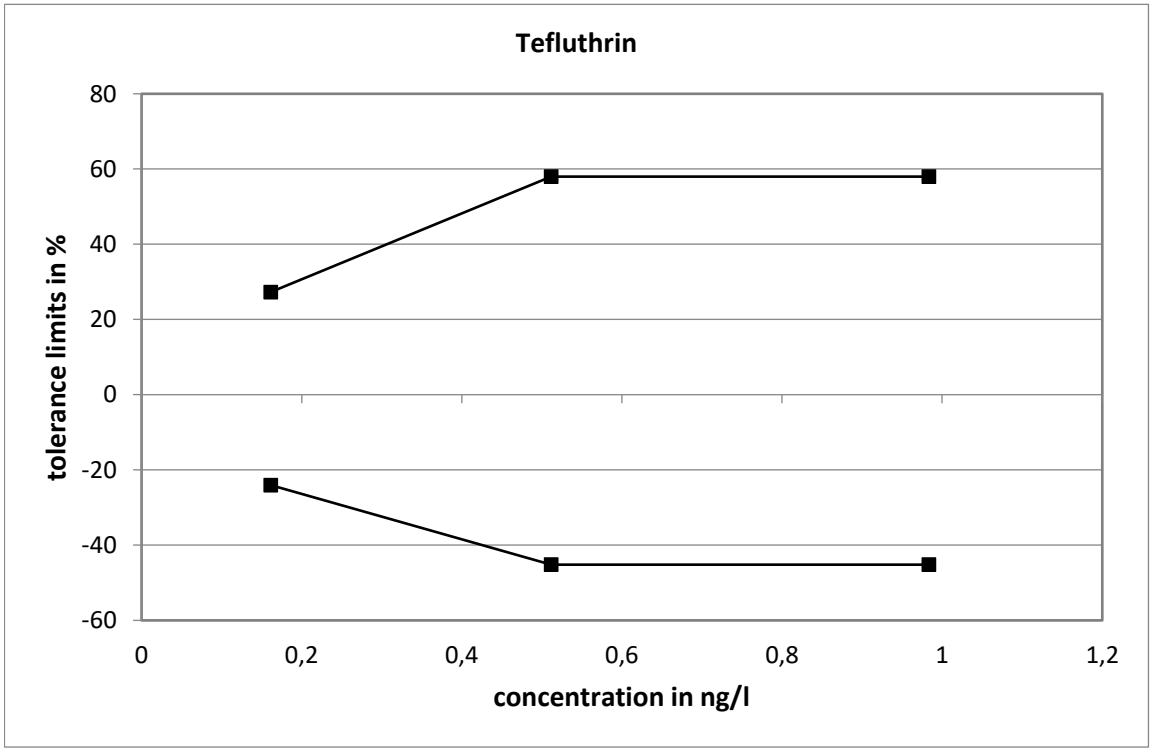
Recovery and matrix content



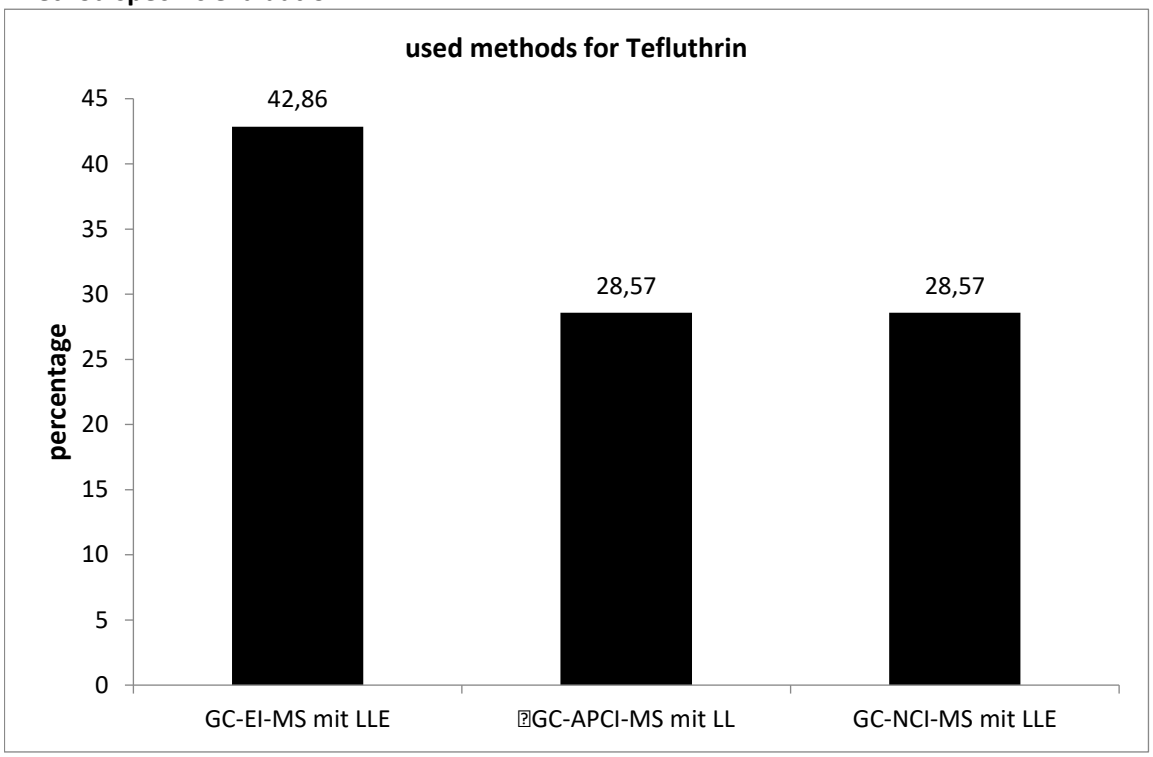
calculated matrix content: 0 ng/l average recovery: 90,7%

Relative standard deviation and tolerance limits

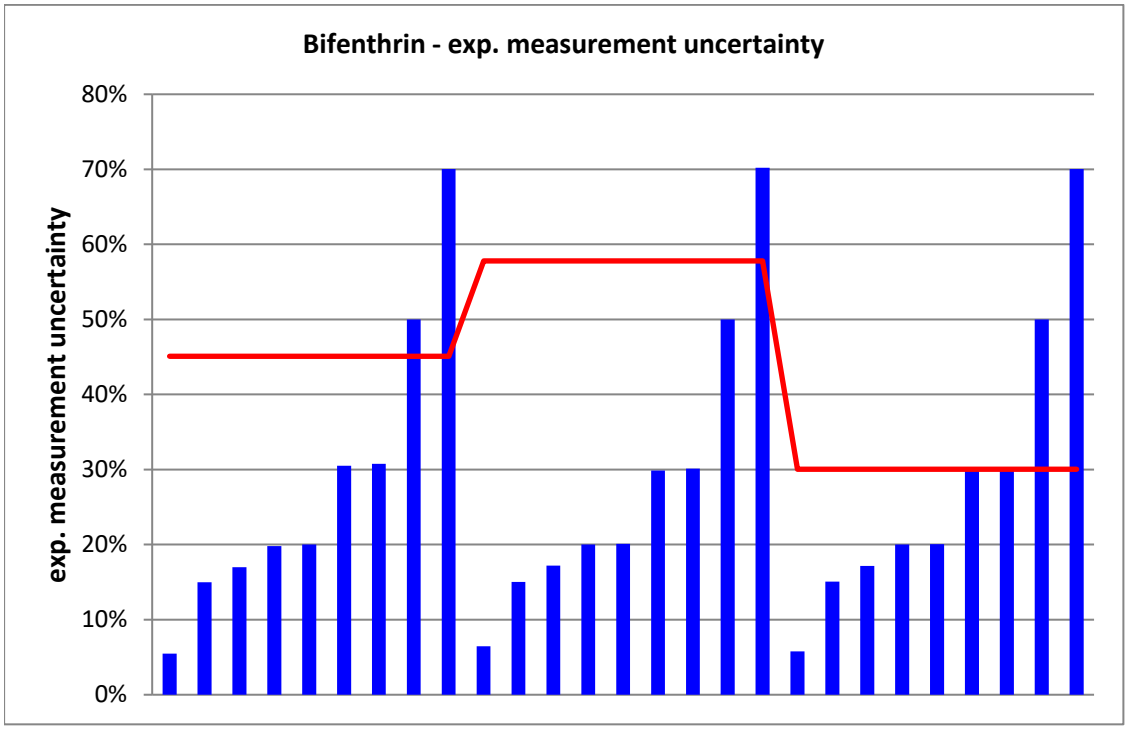


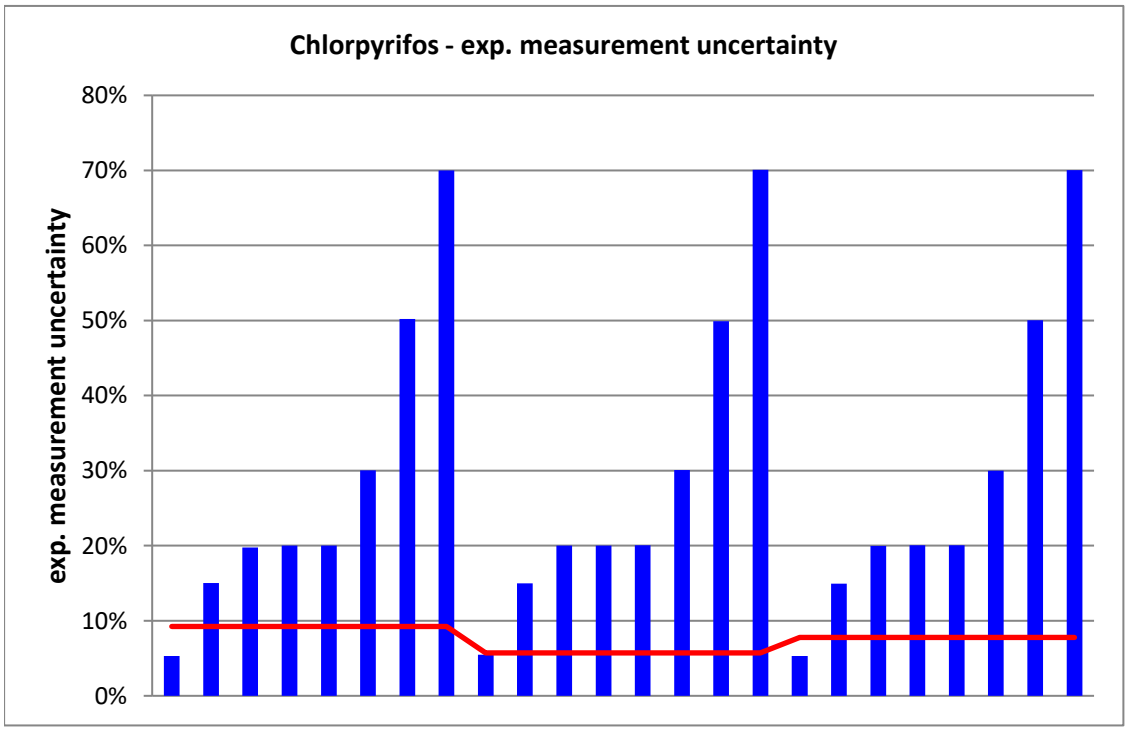


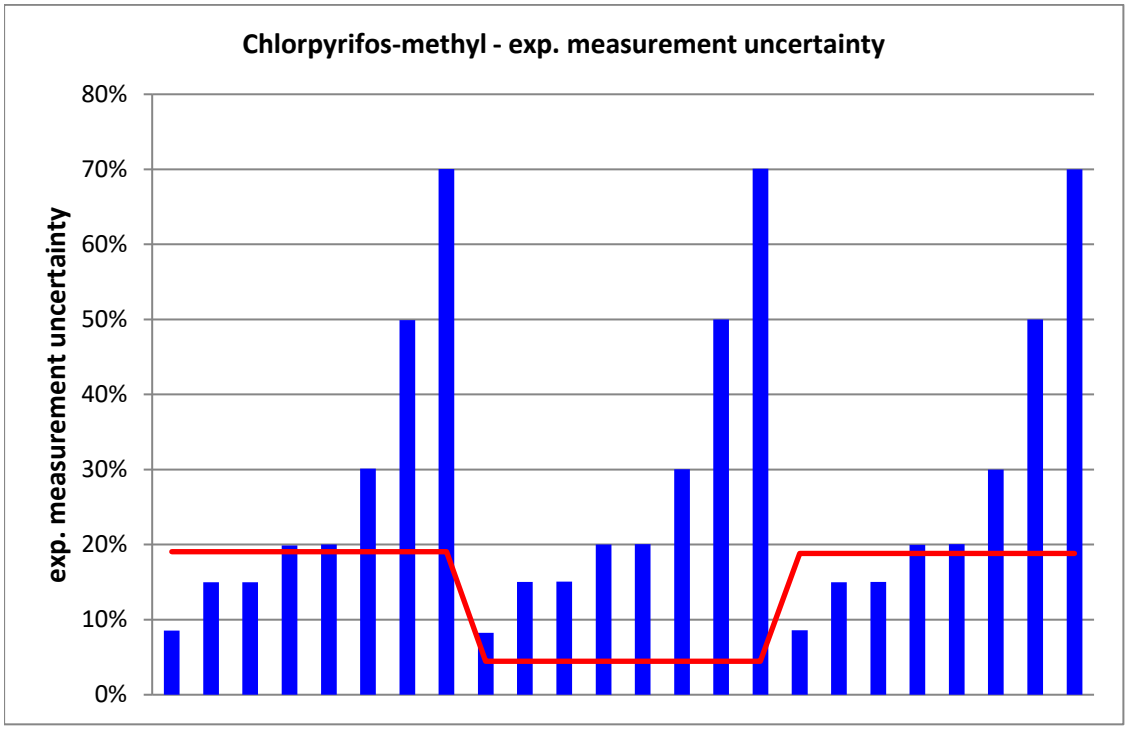
Method specific evaluation

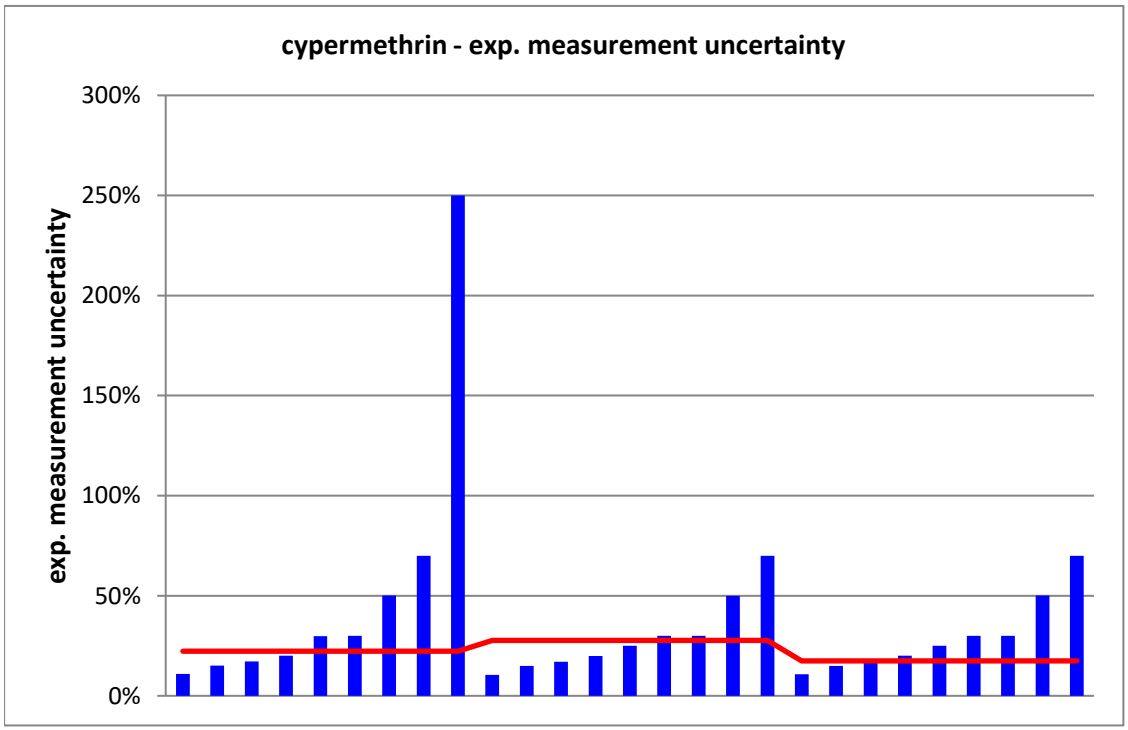


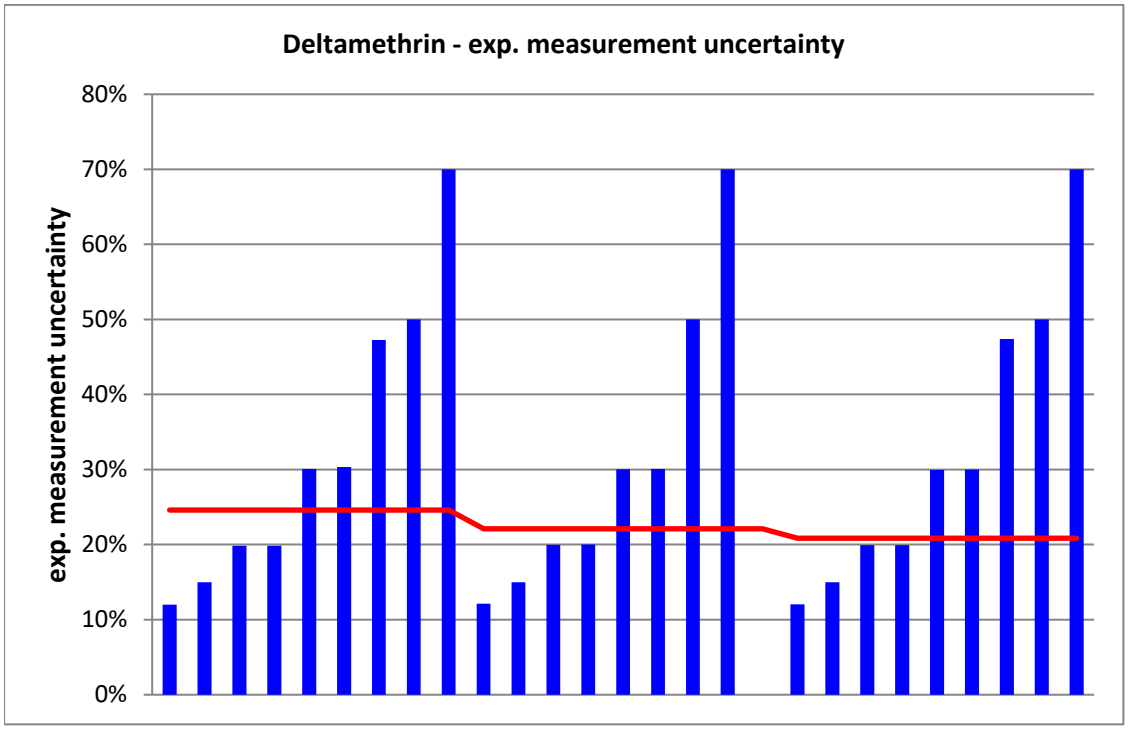
Due to the small number of participants, a comparison of methods is not meaningful.

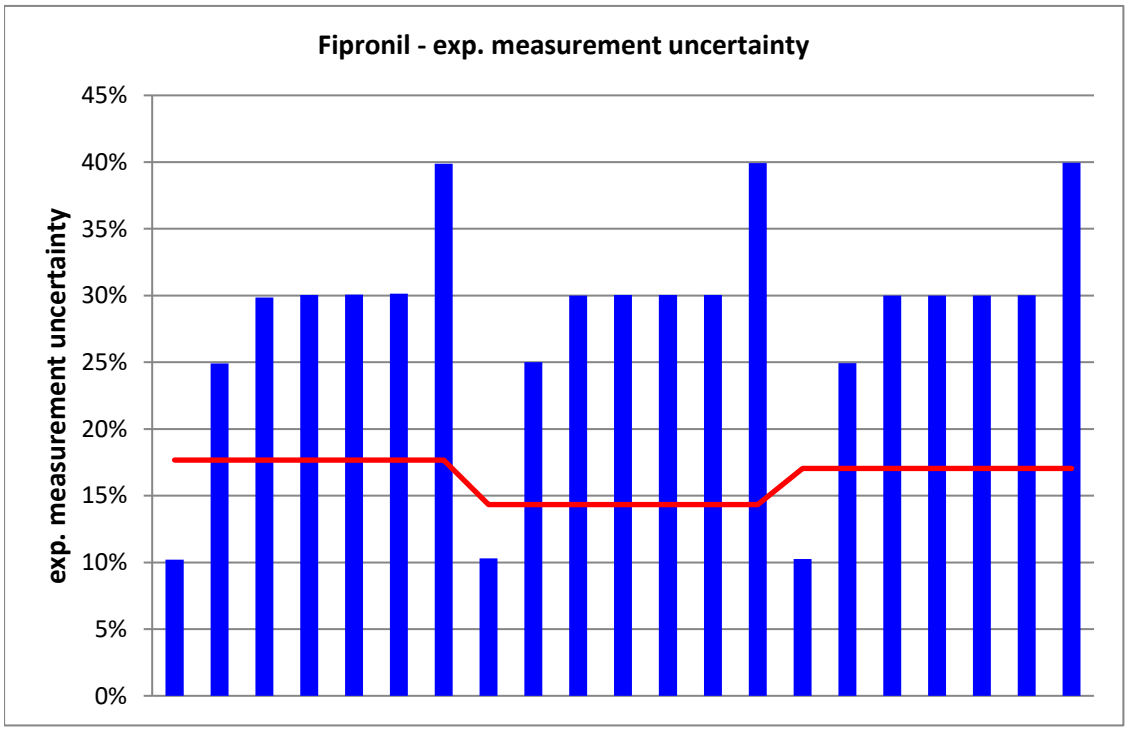

Bifenthrin - exp. measurement uncertainty
exp. measurement uncertainty
80%
70%
60%
50%
40%
30%
20%
10%
0%

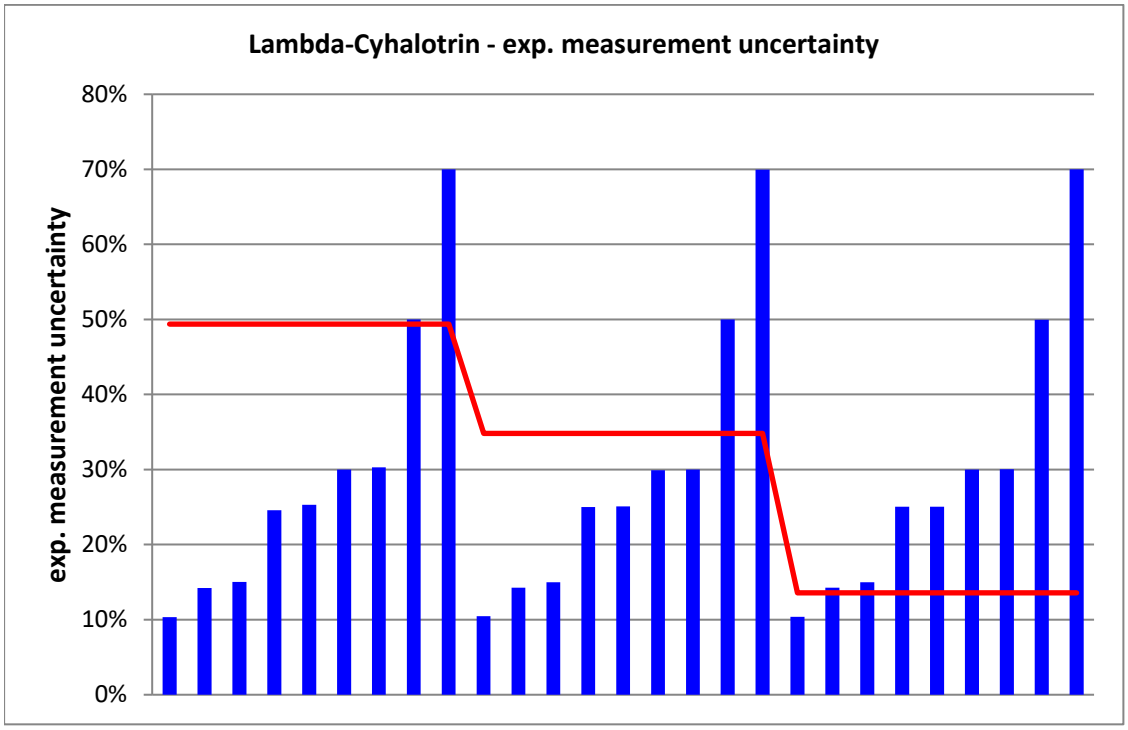

Chlorpyrifos - exp. measurement uncertainty
exp. measurement uncertainty
80%
70%
60%
50%
40%
30%
20%
10%
0%

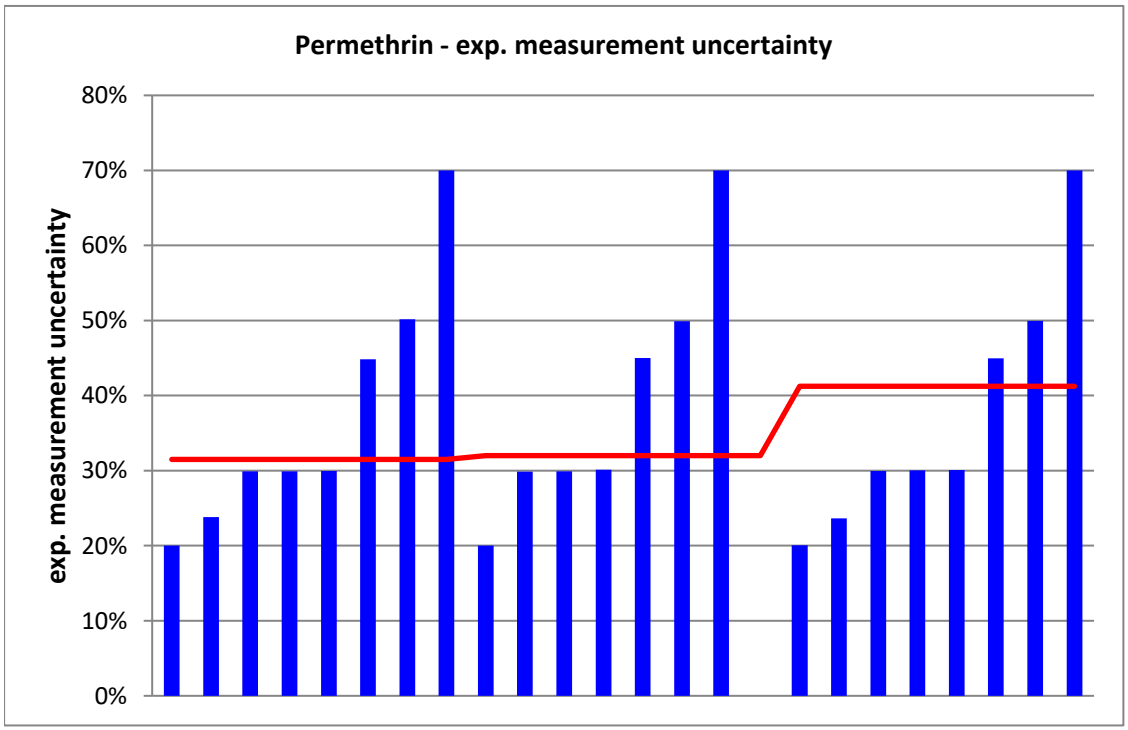

Chlorpyrifos-methyl - exp. measurement uncertainty
exp. measurement uncertainty
80%
70%
60%
50%
40%
30%
20%
10%
0%

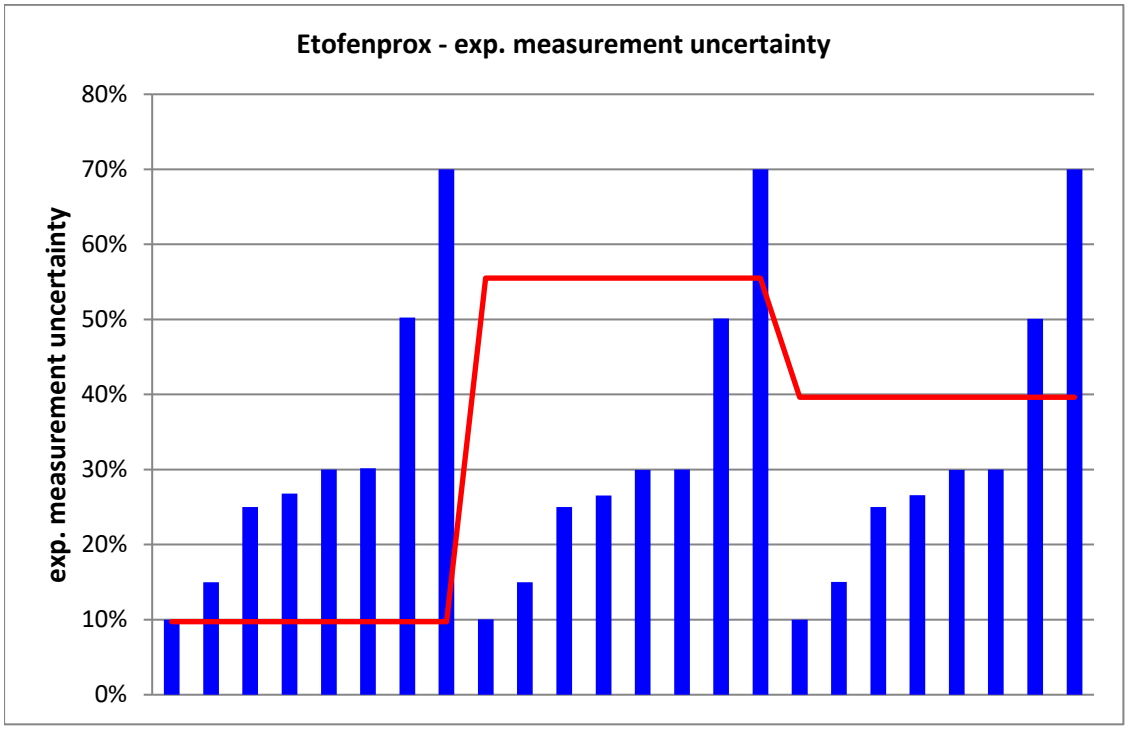

cypermethrin - exp. measurement uncertainty
exp. measurement uncertainty
300%
250%
200%
150%
100%
50%
0%

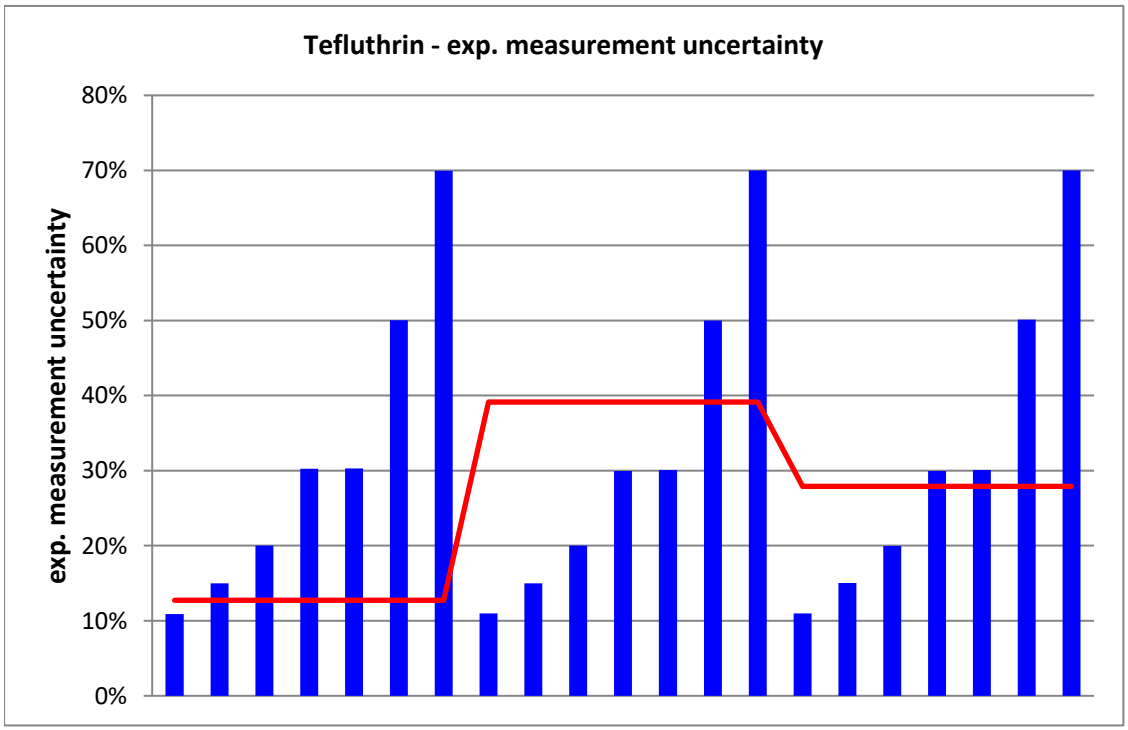

Deltamethrin - exp. measurement uncertainty
exp. measurement uncertainty
80%
70%
60%
50%
40%
30%
20%
10%
0%


Fipronil - exp. measurement uncertainty
exp. measurement uncertainty
45%
40%
35%
30%
25%
20%
15%
10%
5%
0%


Lambda-Cyhalotrin - exp. measurement uncertainty
exp. measurement uncertainty
80%
70%
60%
50%
40%
30%
20%
10%
0%


Permethrin - exp. measurement uncertainty
exp. measurement uncertainty
80%
70%
60%
50%
40%
30%
20%
10%
0%

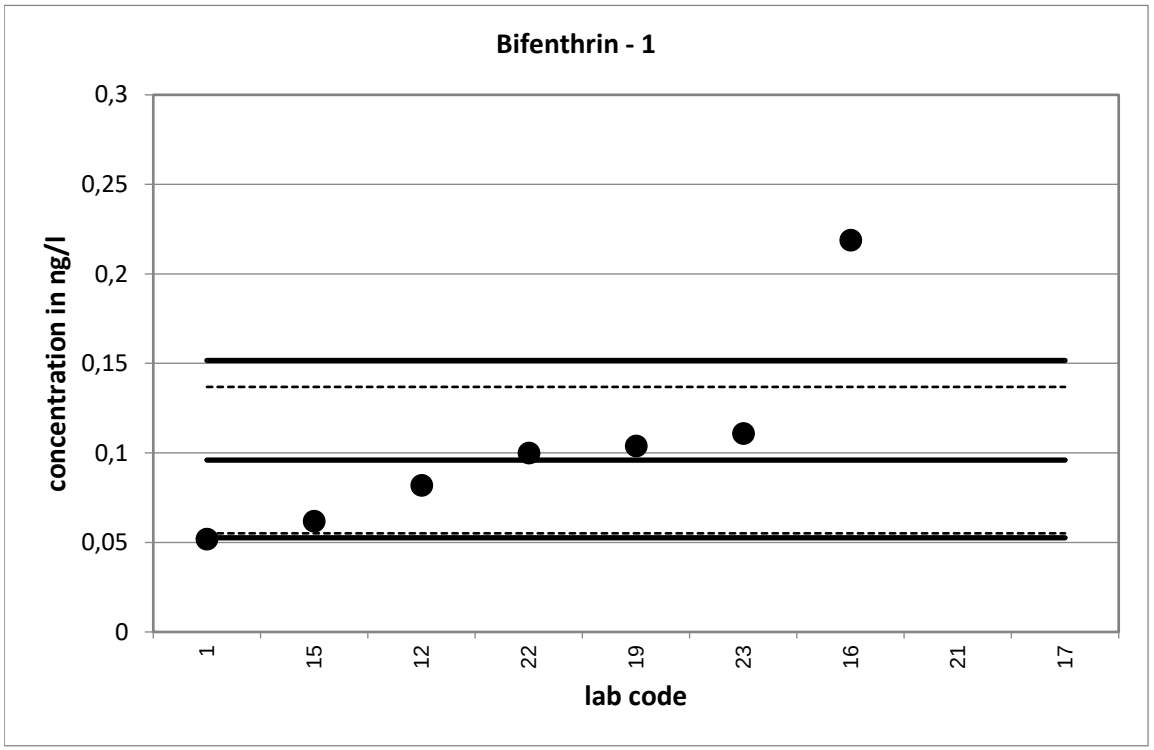

Etofenprox - exp. measurement uncertainty
exp. measurement uncertainty
80%
70%
60%
50%
40%
30%
20%
10%
0%


Tefluthrin - exp. measurement uncertainty
exp. measurement uncertainty
80%
70%
60%
50%
40%
30%
20%
10%
0%

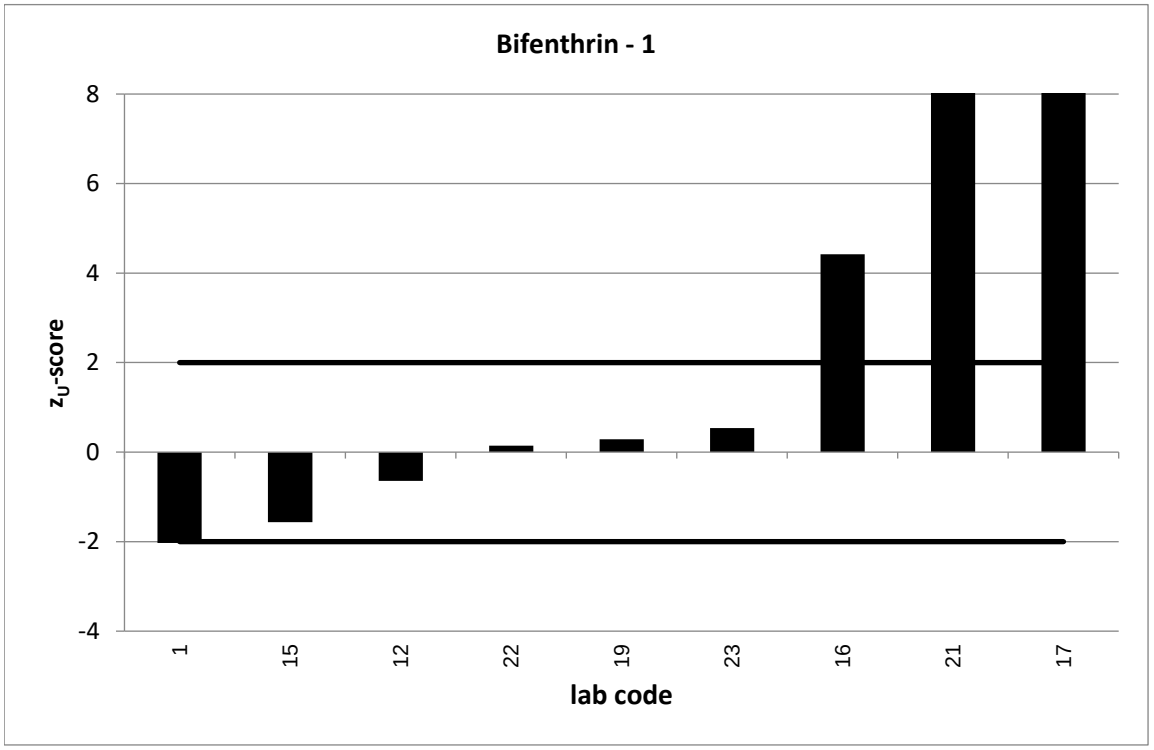
PT 4/24 - Pyrethroids		Bifenthrin - 1			
assigned value [ng/l]*		0,09599	± 0,04089		
upper tolerance limit [ng/l]		0,1516			
lower tolerance limit [ng/l]		0,05261			
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,052	0,016	-2,0	-2,0	s
12	0,082	0,025	-0,6	-0,6	s
15	0,062	0,012	-1,6	-1,6	s
16	0,219	0,012	5,8	4,4	u
17	0,774	0,542	2,5	24,4	u
19	0,104	0,016	0,4	0,3	s
21	0,488	0,244	3,2	14,1	u
22	0,1	0,017	0,2	0,1	s
23	0,111	0,022	0,6	0,5	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

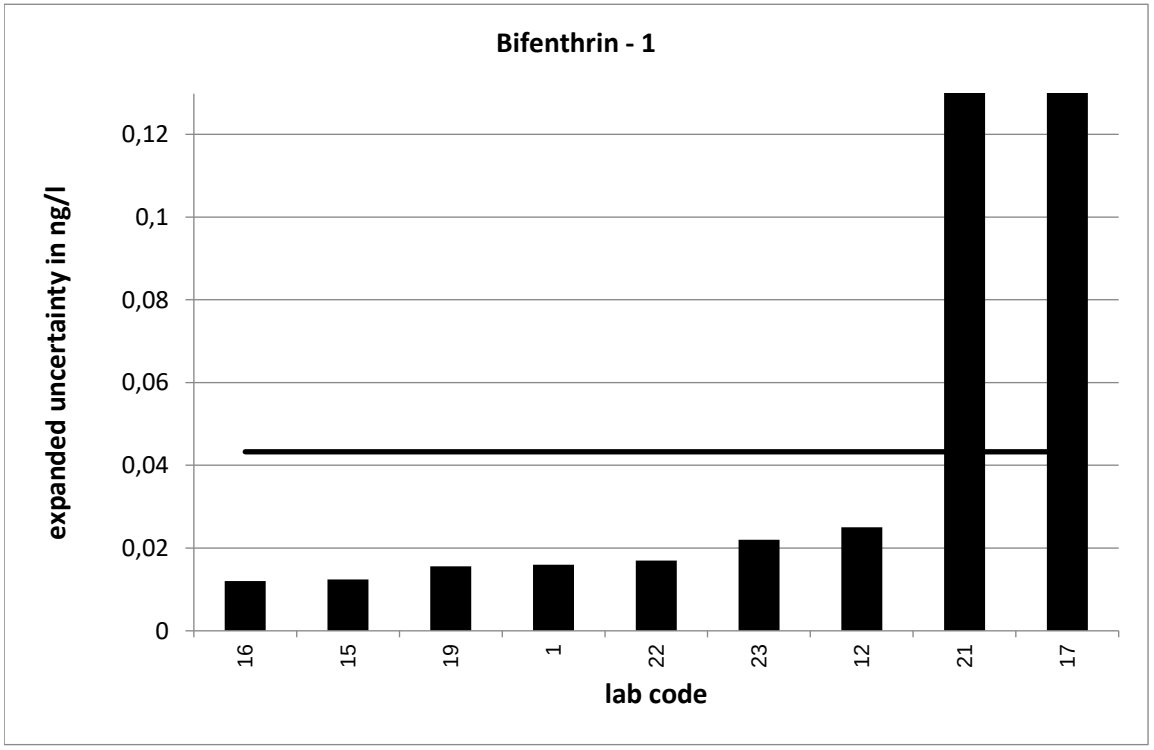
** s = satisfactory, q = questionable, u = unsatisfactory



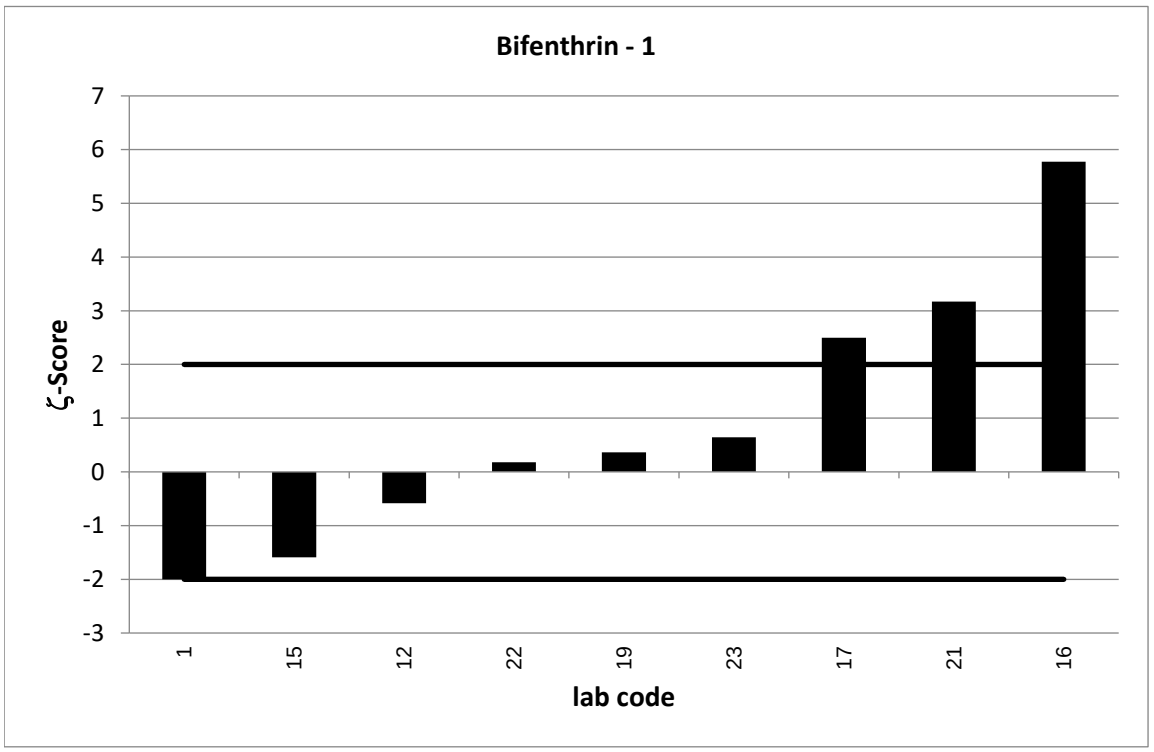
Strongly deviating values are not shown in the diagram.



Strongly deviating values are not correctly shown in the diagram.



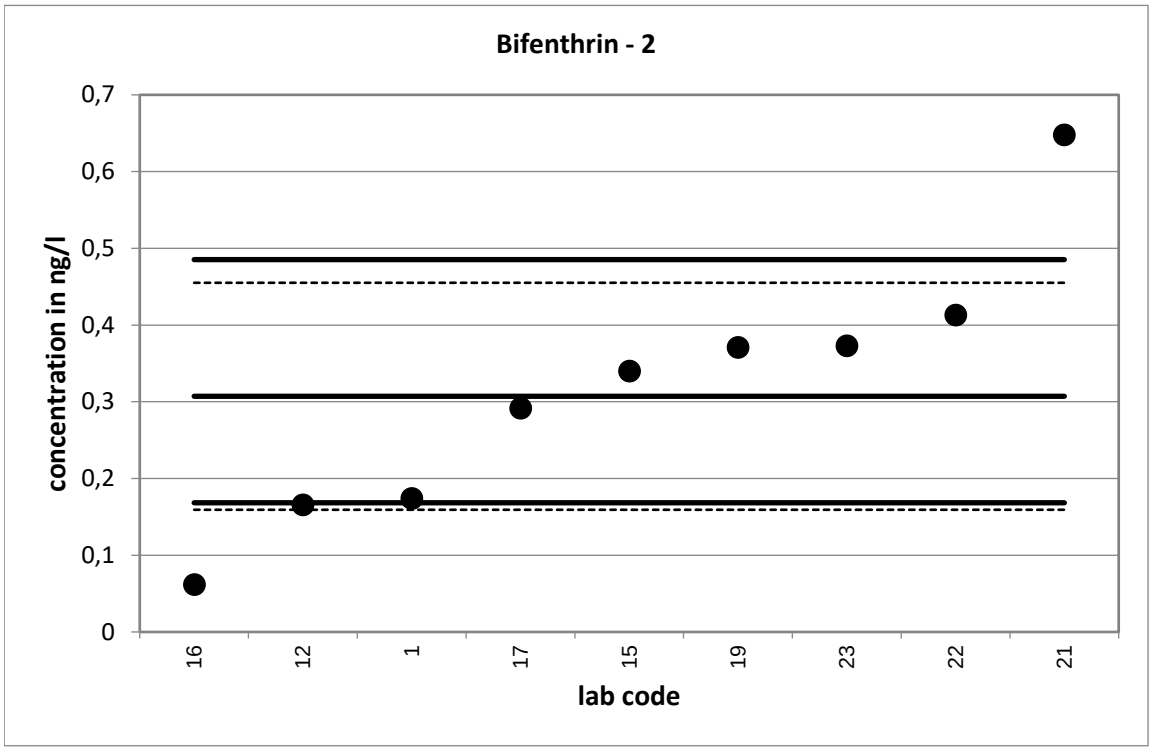
Strongly deviating values are not correctly shown in the diagram.



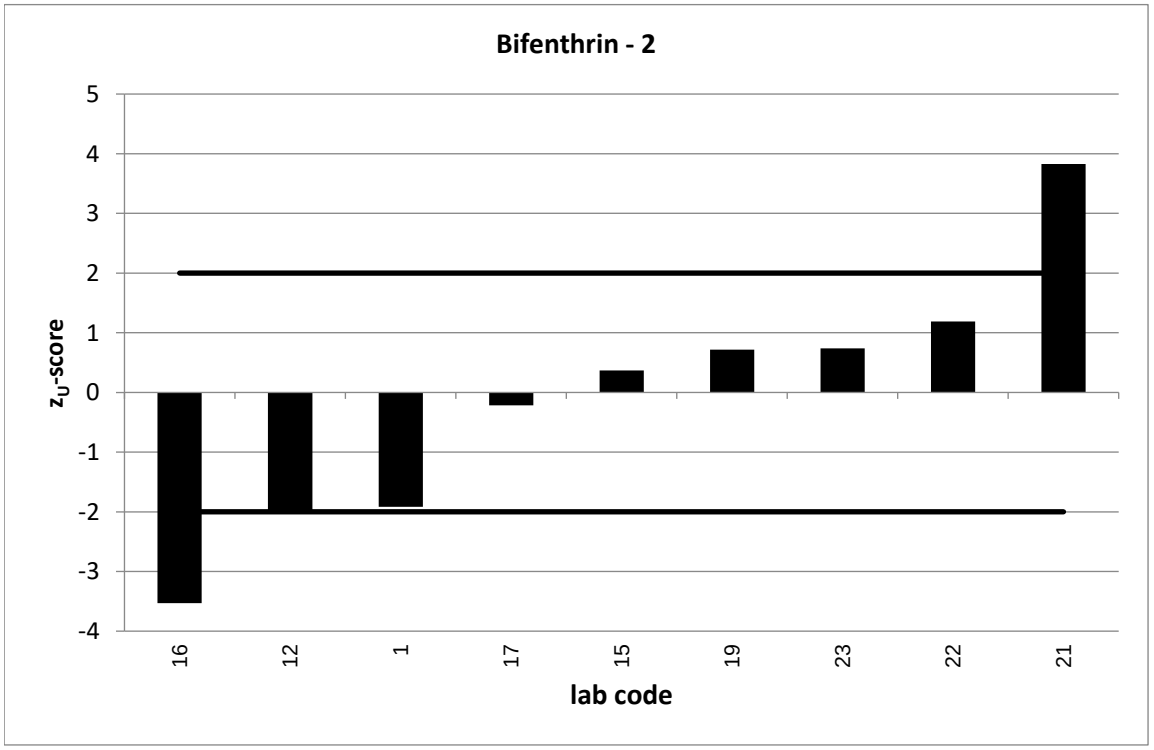
PT 4/24 - Pyrethroids		Bifenthrin - 2			
assigned value [ng/l]*		0,3072	± 0,1479		
upper tolerance limit [ng/l]		0,4853			
lower tolerance limit [ng/l]		0,1684			
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,174	0,052	-1,7	-1,9	s
12	0,166	0,05	-1,8	-2,0	s
15	0,34	0,068	0,4	0,4	s
16	0,062	0,004	-3,3	-3,5	u
17	0,292	0,205	-0,1	-0,2	s
19	0,371	0,056	0,8	0,7	s
21	0,648	0,324	1,9	3,8	u
22	0,413	0,071	1,3	1,2	s
23	0,373	0,075	0,8	0,7	s

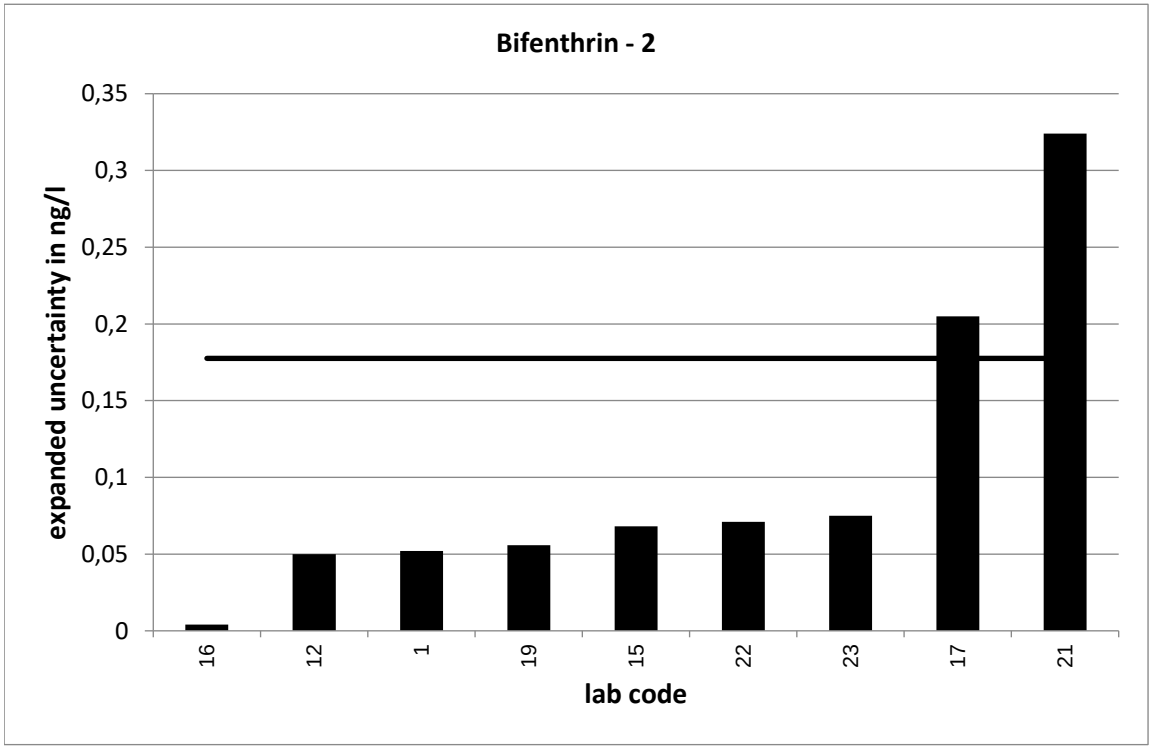
* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

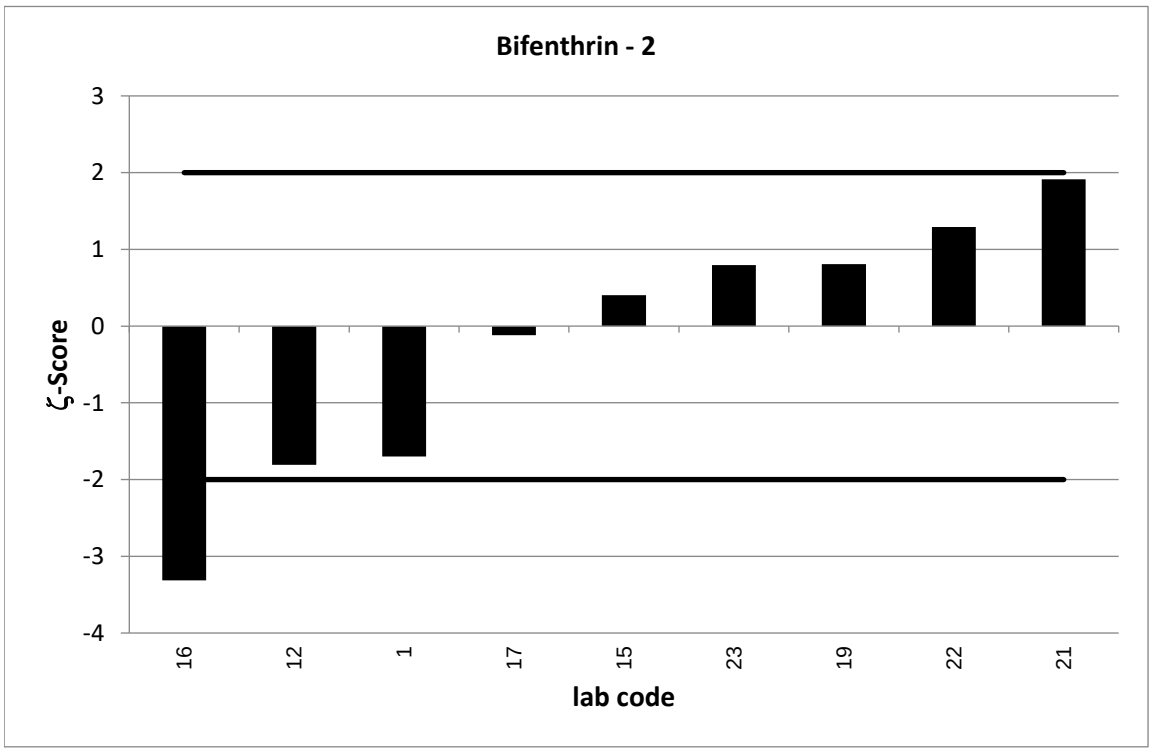
** s = satisfactory, q = questionable, u = unsatisfactory



Strongly deviating values are not shown in the diagram.



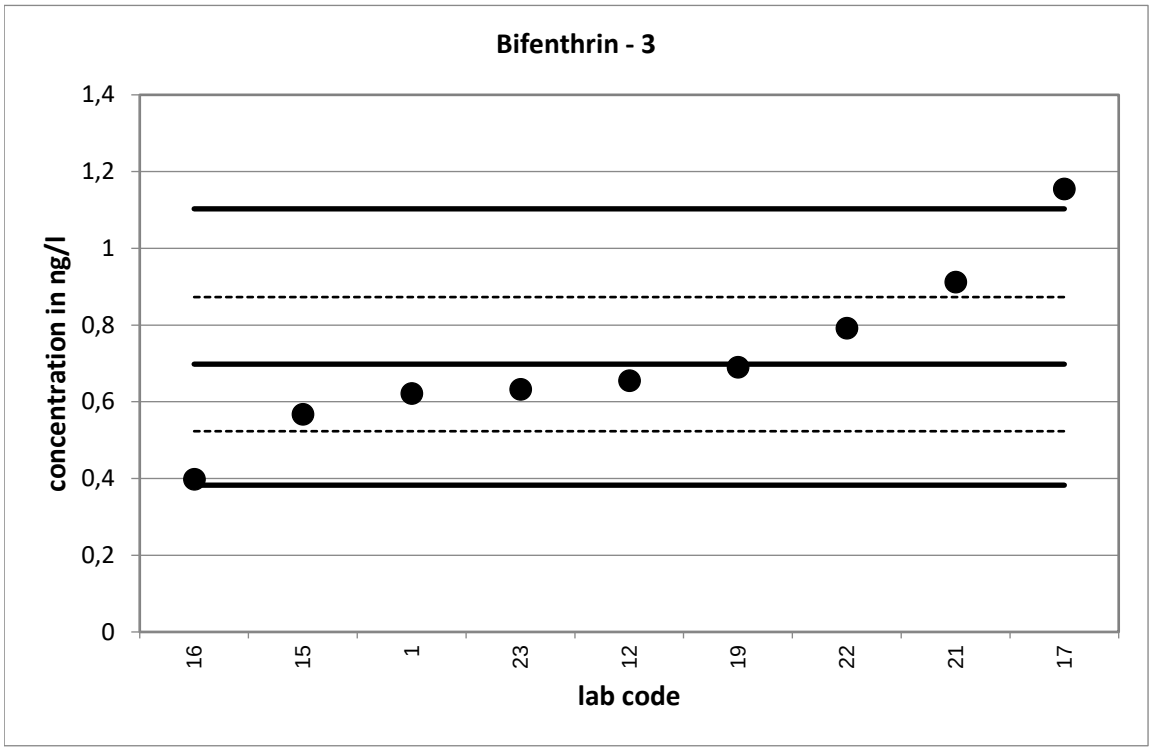

Bifenthrin - 2
expanded uncertainty in ng/l
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
16
12
1
19
15
22
23
17
21
lab code


Bifenthrin - 2
ζ-Score
3
2
1
0
-1
-2
-3
-4
16
12
1
17
15
23
19
22
21
lab code

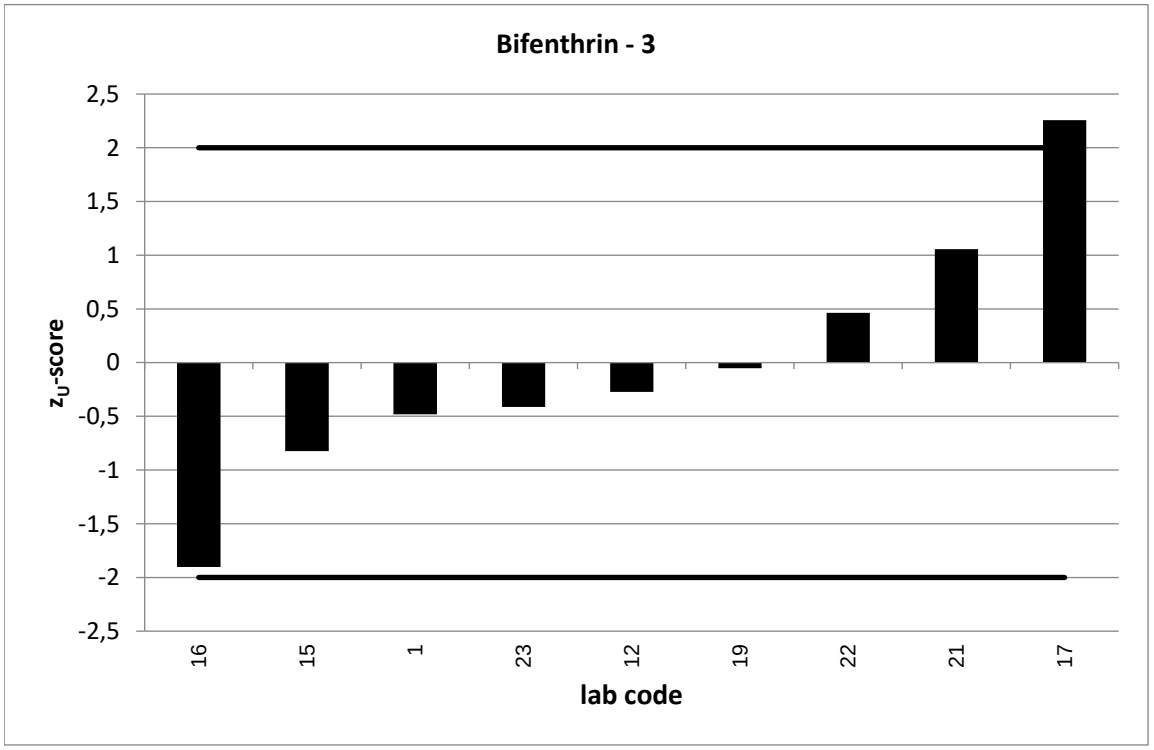
PT 4/24 - Pyrethroids		Bifenthrin - 3			
assigned value [ng/l]*			0,6981	± 0,1748	
upper tolerance limit [ng/l]			1,103		
lower tolerance limit [ng/l]			0,3826		
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,622	0,187	-0,6	-0,5	s
12	0,655	0,196	-0,3	-0,3	s
15	0,568	0,114	-1,2	-0,8	s
16	0,398	0,023	-3,4	-1,9	s
17	1,155	0,809	1,1	2,3	q
19	0,69	0,104	-0,1	-0,1	s
21	0,912	0,456	0,9	1,1	s
22	0,792	0,136	0,8	0,5	s
23	0,633	0,127	-0,6	-0,4	s

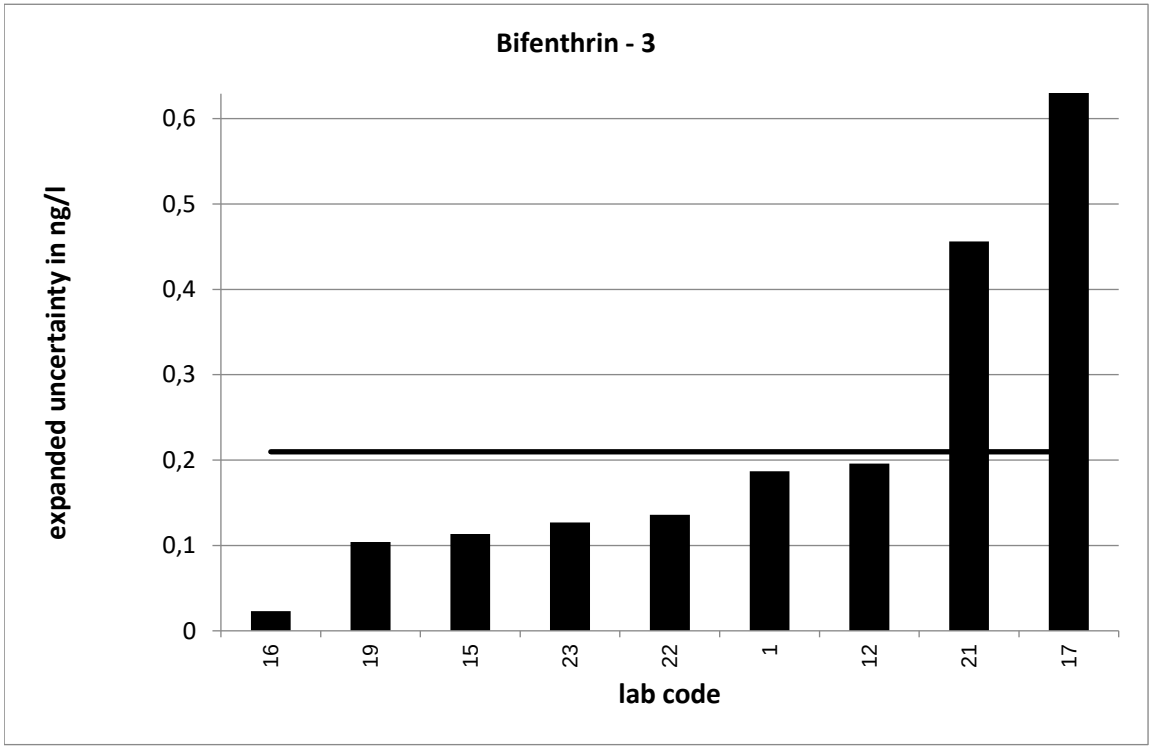
* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

** s = satisfactory, q = questionable, u = unsatisfactory

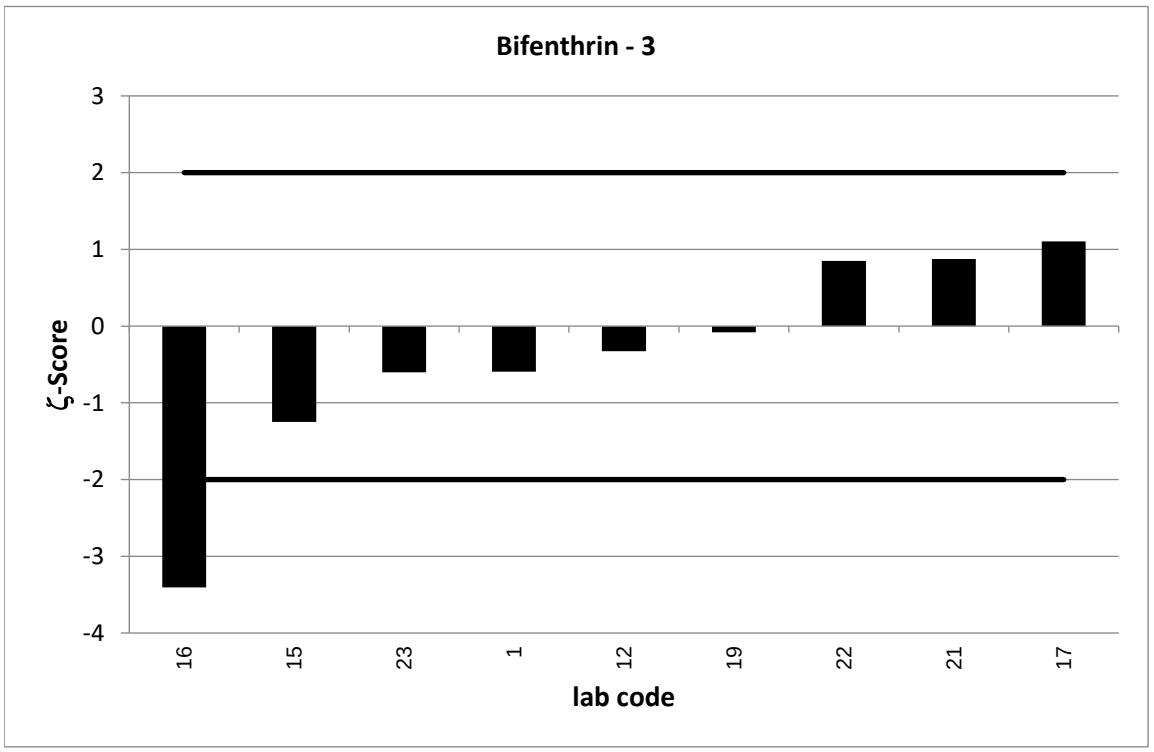


Strongly deviating values are not shown in the diagram.





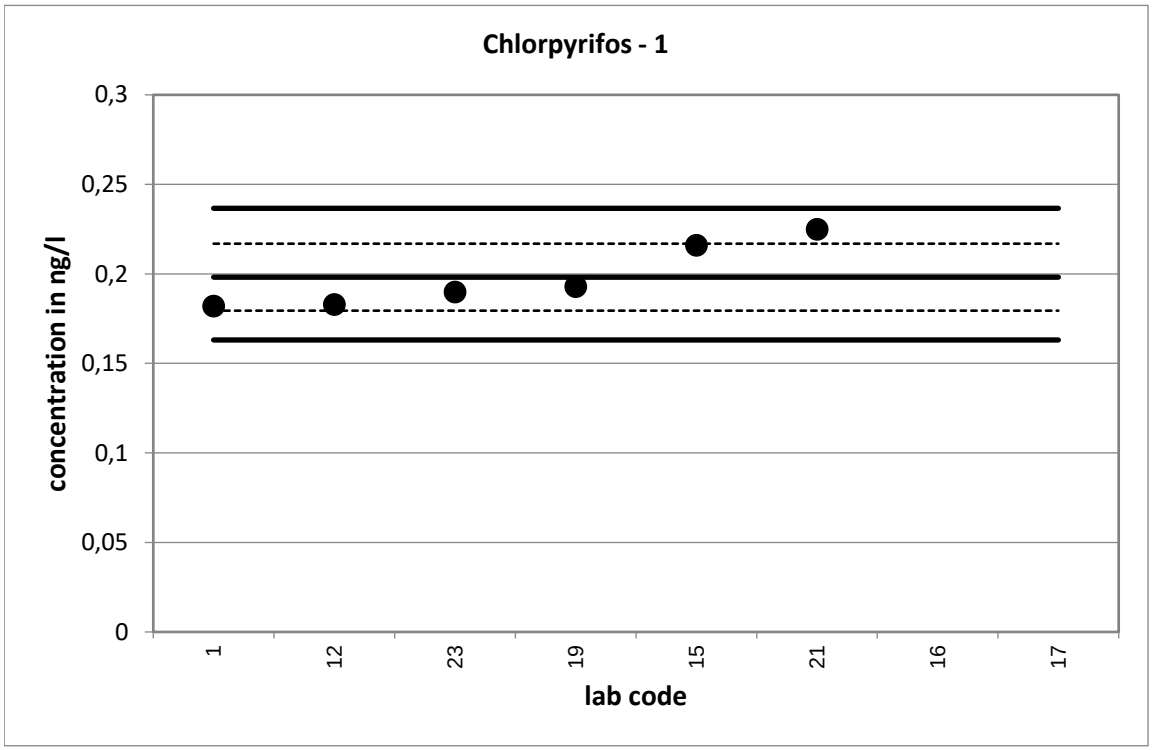
Strongly deviating values are not correctly shown in the diagram.



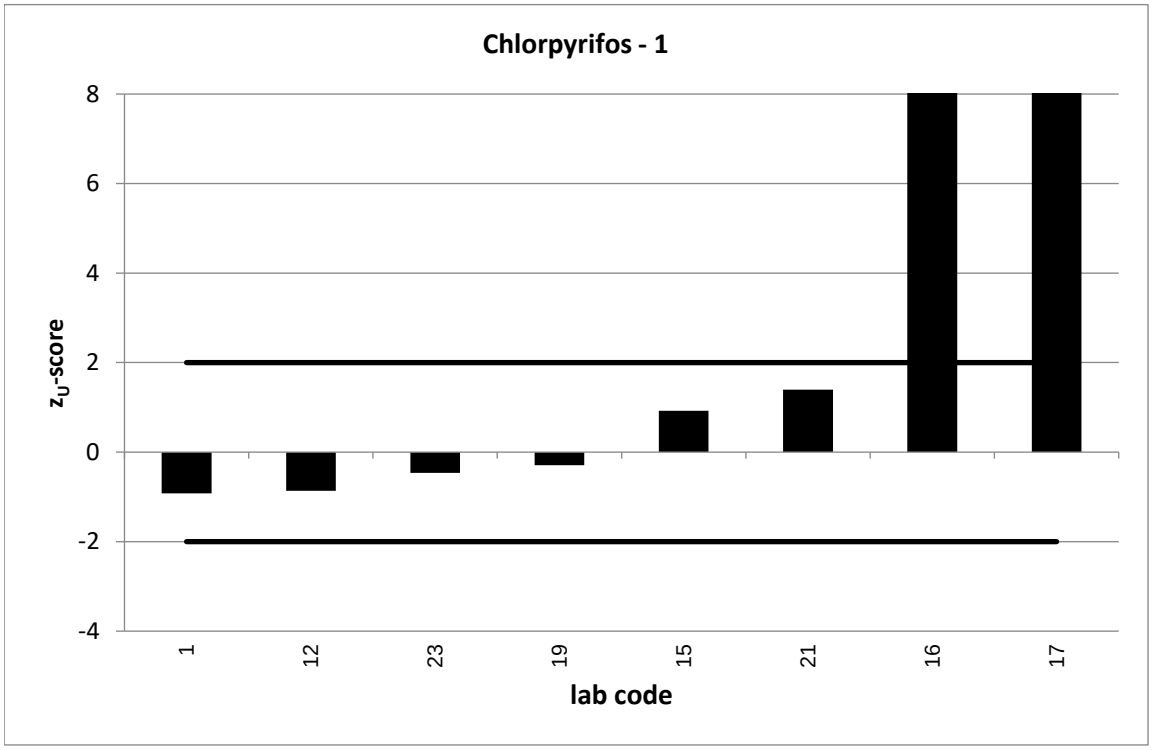
PT 4/24 - Pyrethroids		Chlorpyrifos - 1			
assigned value [ng/l]*		0,1982	± 0,0187		
upper tolerance limit [ng/l]		0,2366			
lower tolerance limit [ng/l]		0,1631			
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,182	0,036	-0,8	-0,9	s
12	0,183	0,055	-0,5	-0,9	s
15	0,216	0,043	0,8	0,9	s
16	0,547	0,029	20,2	18,1	u
17	1,813	1,269	2,5	84,0	u
19	0,193	0,029	-0,3	-0,3	s
21	0,225	0,113	0,5	1,4	s
23	0,19	0,038	-0,4	-0,5	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

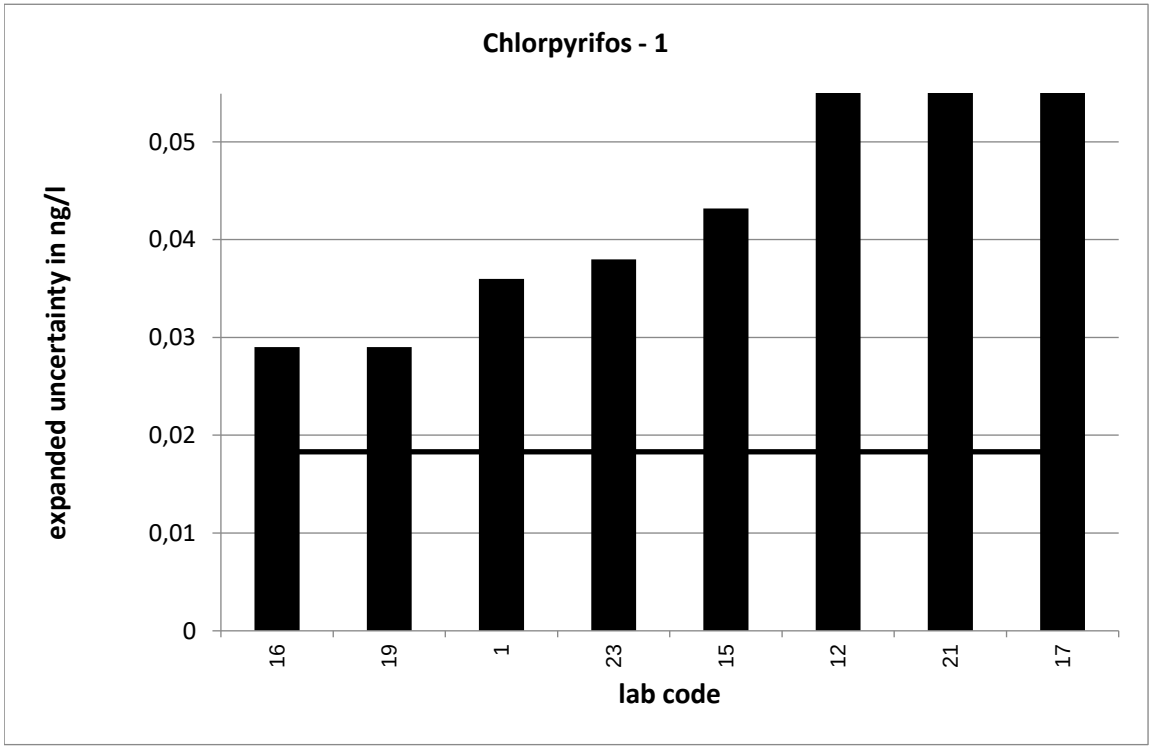
** s = satisfactory, q = questionable, u = unsatisfactory



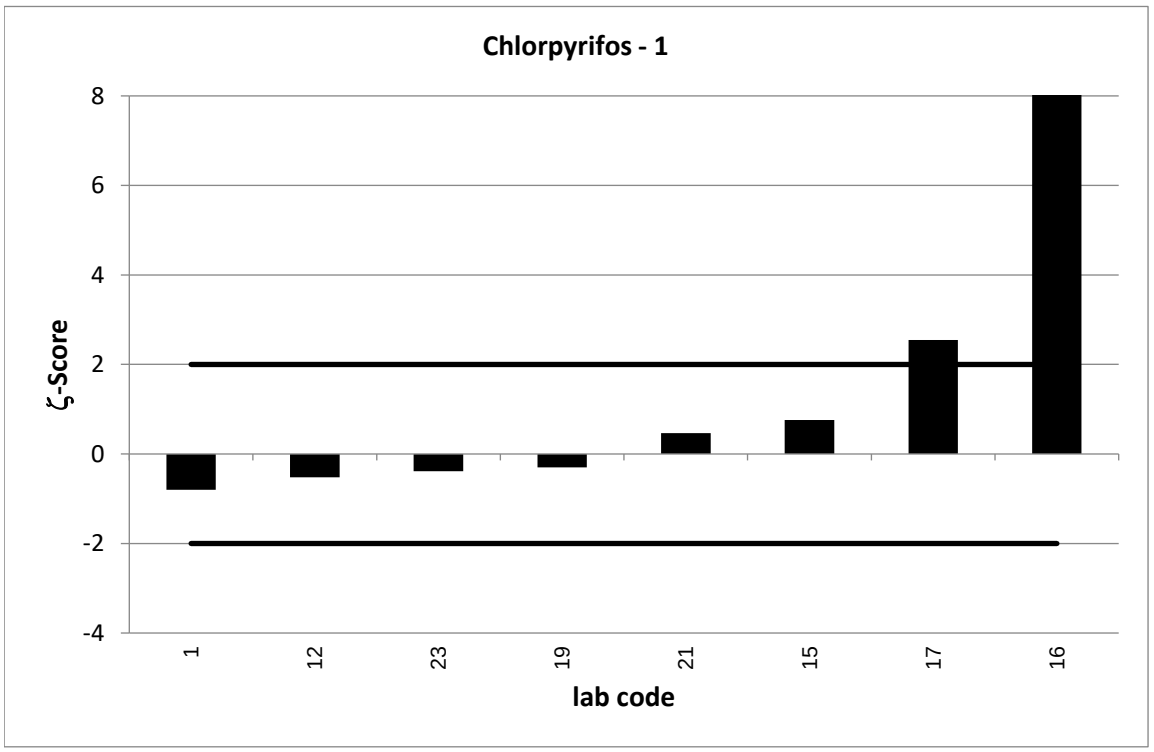
Strongly deviating values are not shown in the diagram.



Strongly deviating values are not correctly shown in the diagram.



Strongly deviating values are not correctly shown in the diagram.

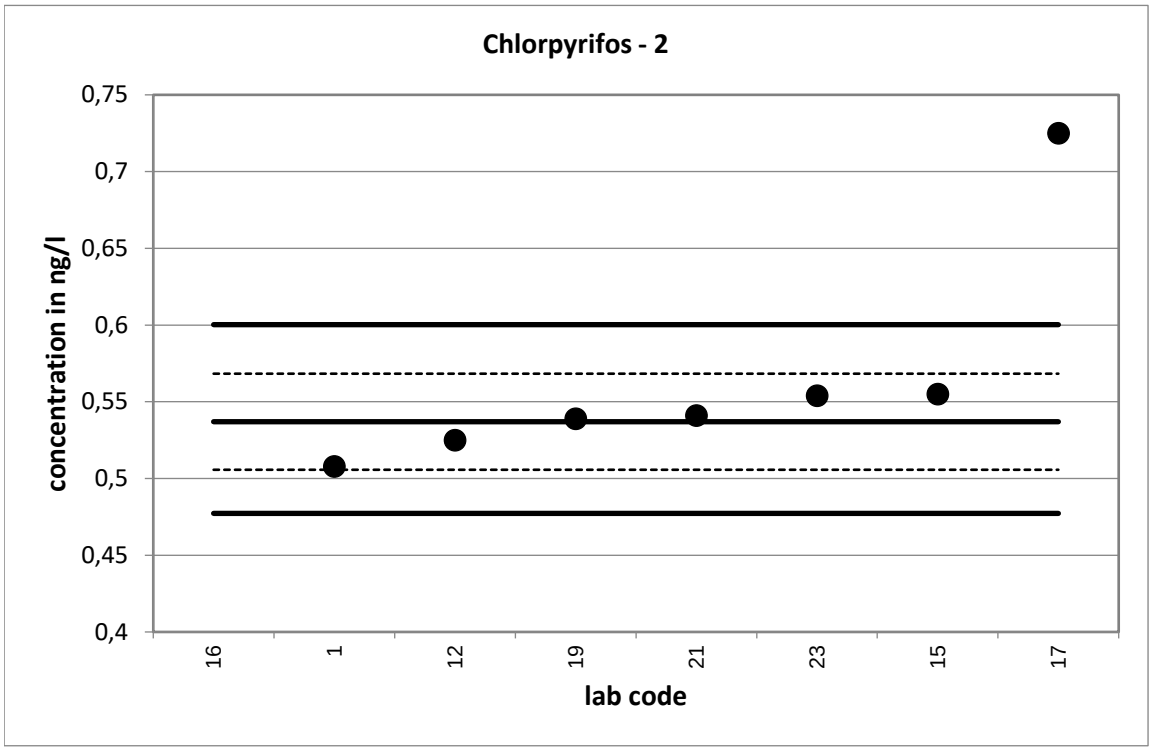


Strongly deviating values are not correctly shown in the diagram.

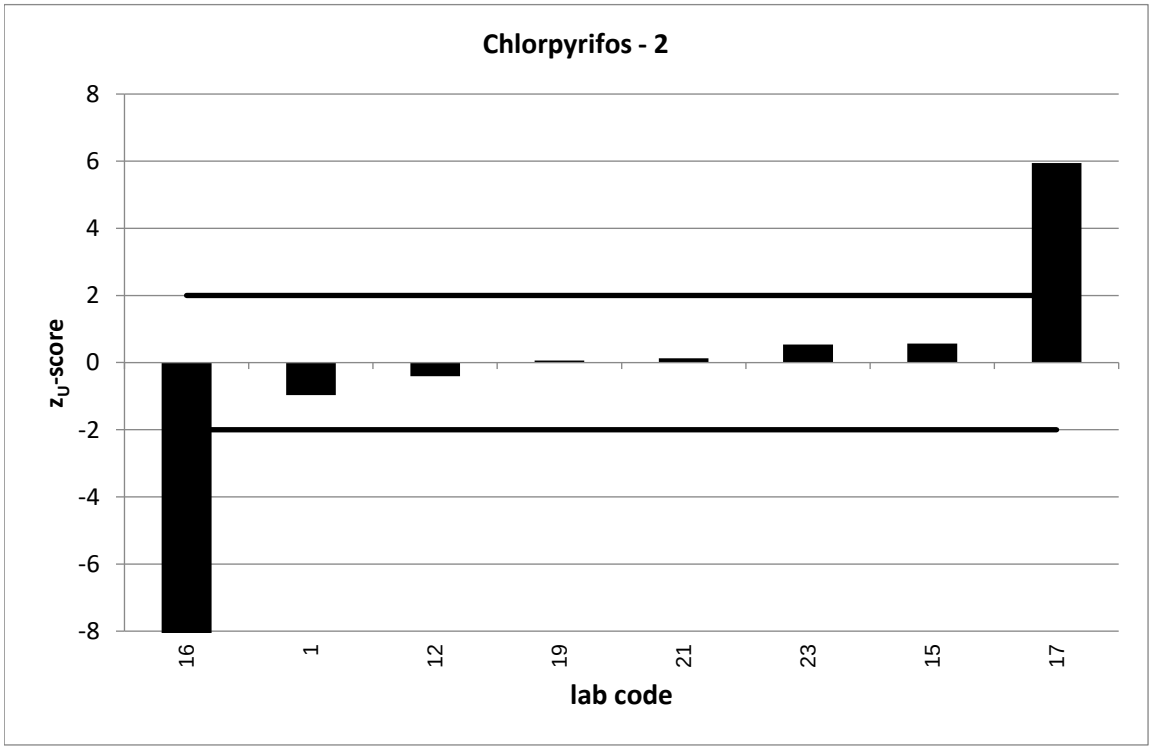
PT 4/24 - Pyrethroids		Chlorpyrifos - 2			
assigned value [ng/l]*			0,537	± 0,0313	
upper tolerance limit [ng/l]			0,6003		
lower tolerance limit [ng/l]			0,4773		
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,508	0,102	-0,5	-1,0	s
12	0,525	0,158	-0,1	-0,4	s
15	0,555	0,111	0,3	0,6	s
16	0,165	0,009	-22,8	-12,5	u
17	0,725	0,508	0,7	5,9	u
19	0,539	0,081	0,0	0,1	s
21	0,541	0,27	0,0	0,1	s
23	0,554	0,111	0,3	0,5	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

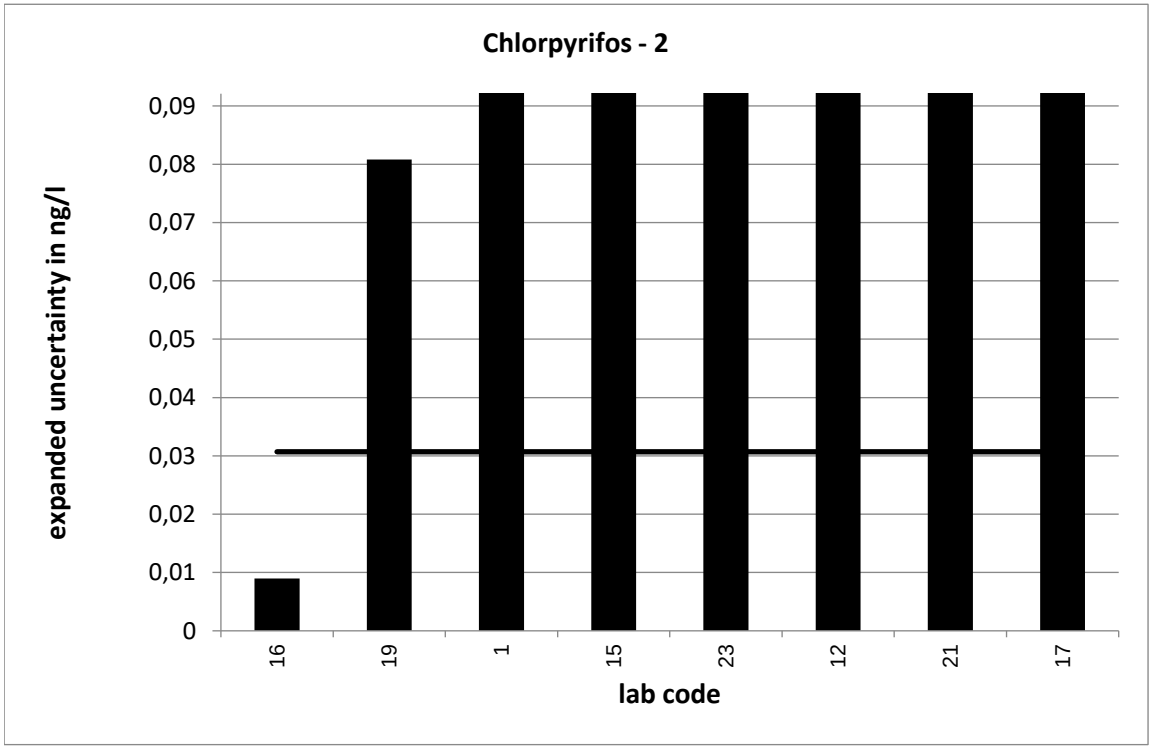
** s = satisfactory, q = questionable, u = unsatisfactory



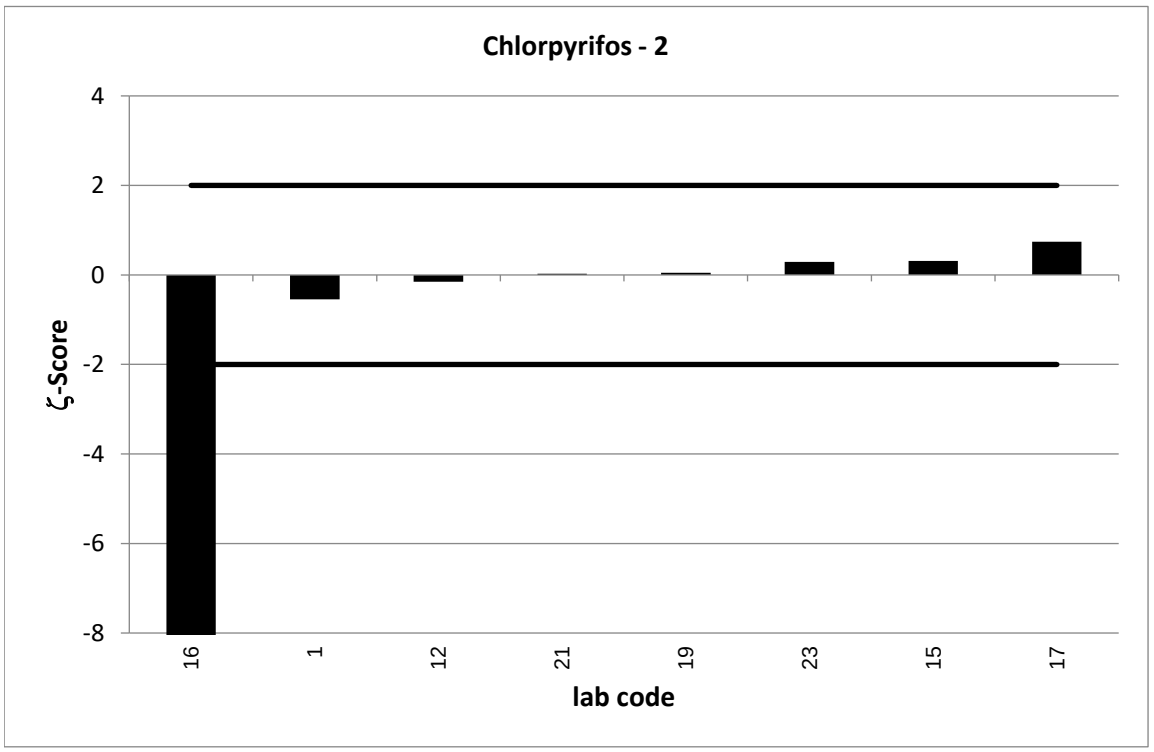
Strongly deviating values are not shown in the diagram.



Strongly deviating values are not correctly shown in the diagram.



Strongly deviating values are not correctly shown in the diagram.

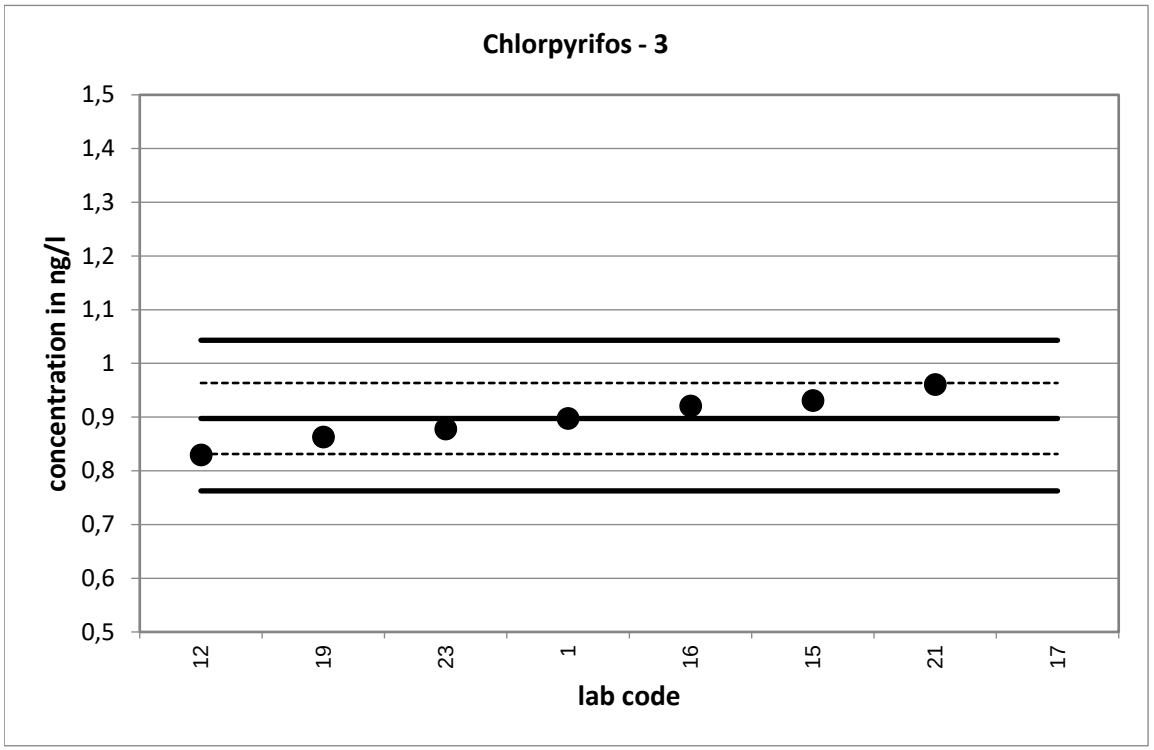


Strongly deviating values are not correctly shown in the diagram.

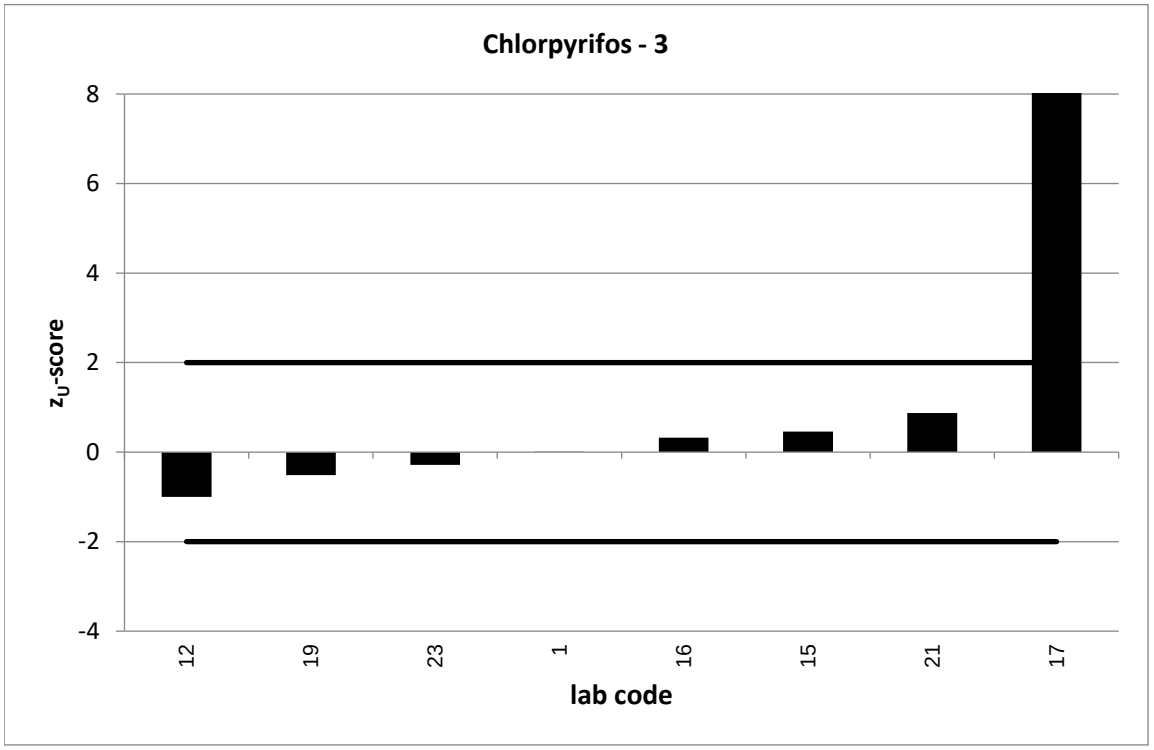
PT 4/24 - Pyrethroids		Chlorpyrifos - 3			
assigned value [ng/l]*			0,8974	± 0,0661	
upper tolerance limit [ng/l]			1,043		
lower tolerance limit [ng/l]			0,7626		
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,898	0,18	0,0	0,0	s
12	0,83	0,249	-0,5	-1,0	s
15	0,931	0,186	0,3	0,5	s
16	0,921	0,049	0,6	0,3	s
17	2,692	1,885	1,9	24,6	u
19	0,863	0,129	-0,5	-0,5	s
21	0,961	0,481	0,3	0,9	s
23	0,878	0,176	-0,2	-0,3	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

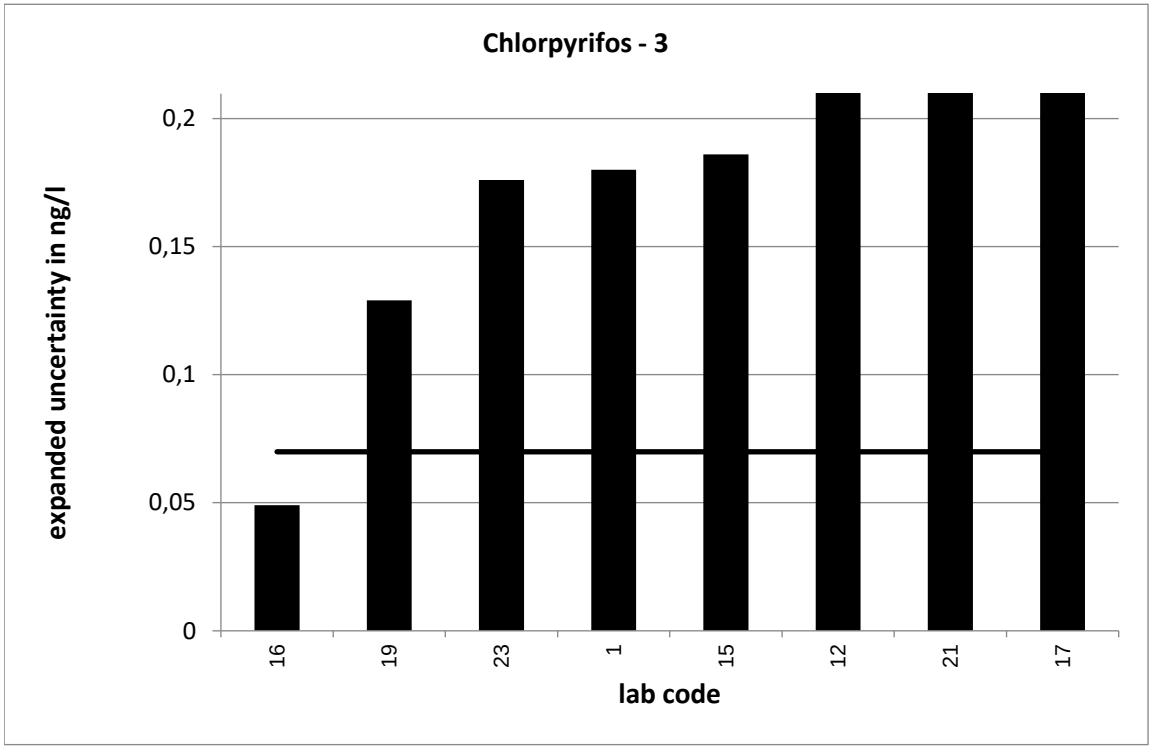
** s = satisfactory, q = questionable, u = unsatisfactory



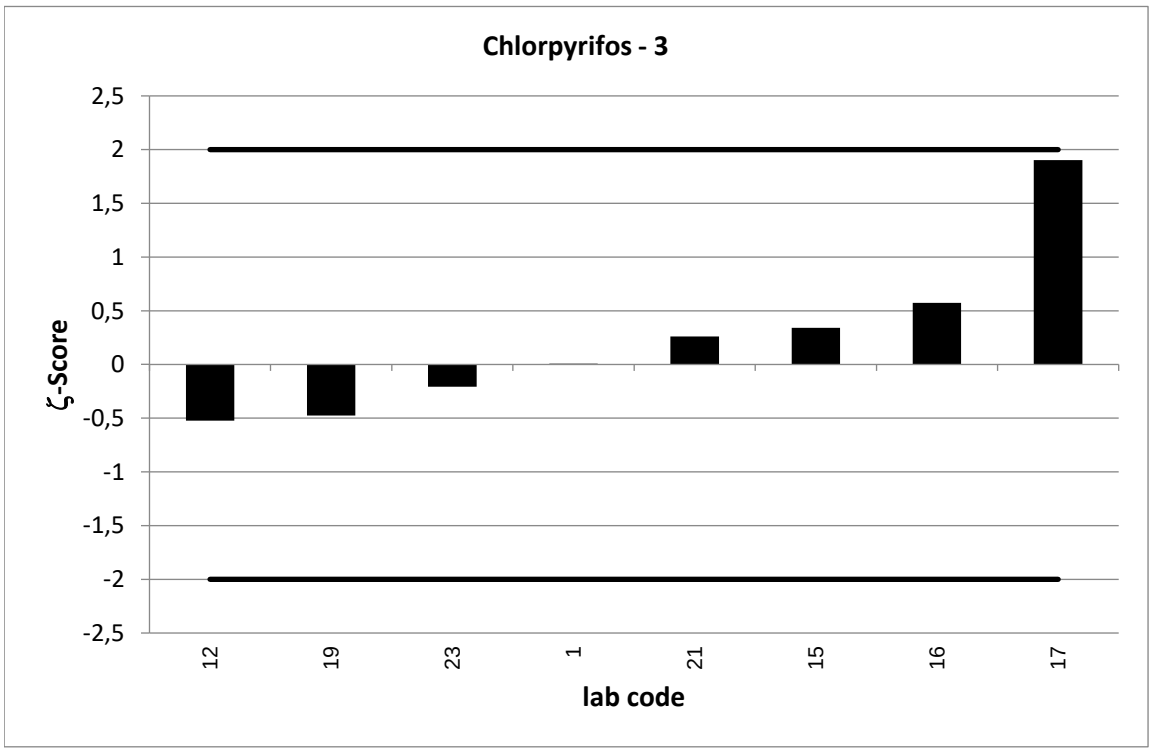
Strongly deviating values are not shown in the diagram.



Strongly deviating values are not correctly shown in the diagram.



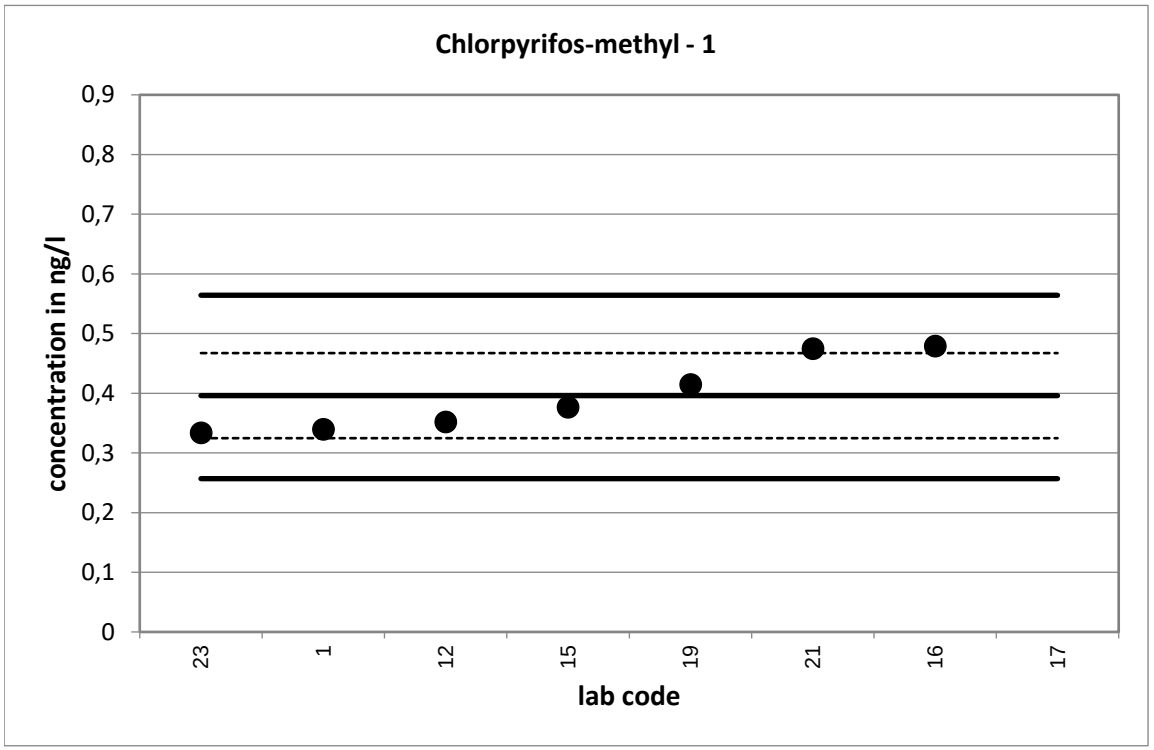
Strongly deviating values are not correctly shown in the diagram.



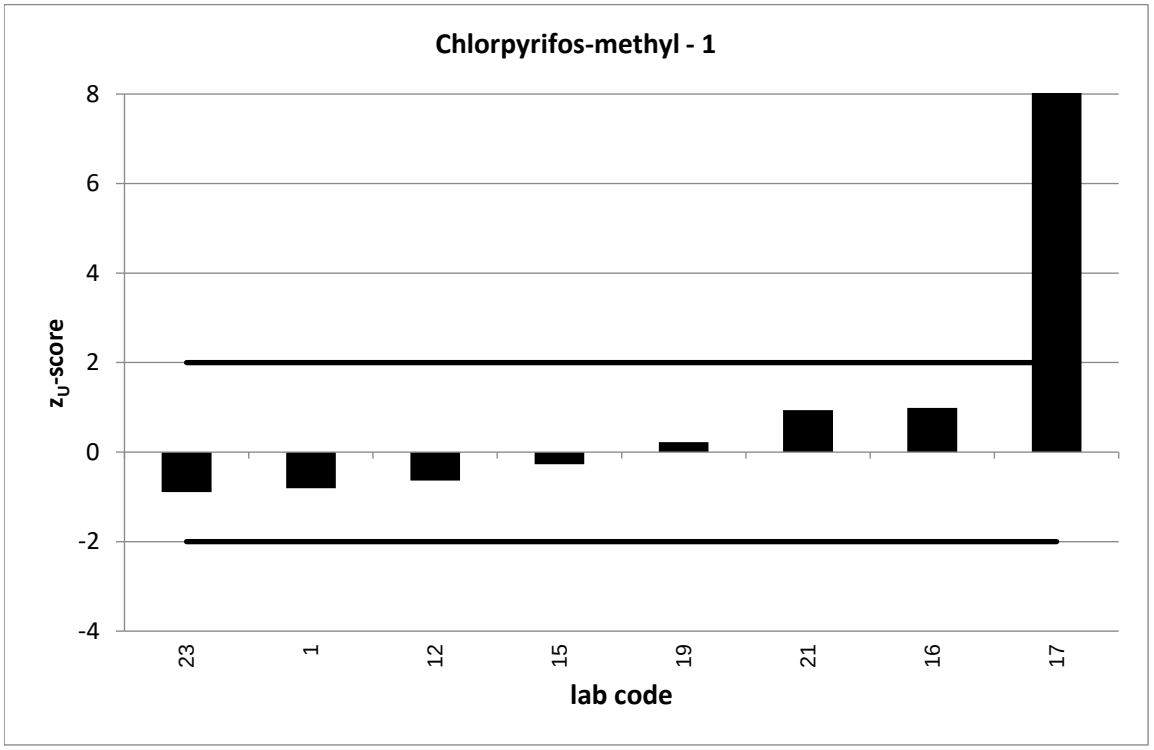
PT 4/24 - Pyrethroids		Chlorpyrifos-methyl - 1			
assigned value [ng/l]*		0,396	± 0,0713		
upper tolerance limit [ng/l]		0,5642			
lower tolerance limit [ng/l]		0,2569			
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,34	0,068	-1,1	-0,8	s
12	0,352	0,106	-0,7	-0,6	s
15	0,377	0,075	-0,4	-0,3	s
16	0,479	0,041	2,0	1,0	s
17	1,541	1,079	2,1	13,6	u
19	0,415	0,062	0,4	0,2	s
21	0,475	0,237	0,6	0,9	s
23	0,334	0,05	-1,4	-0,9	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

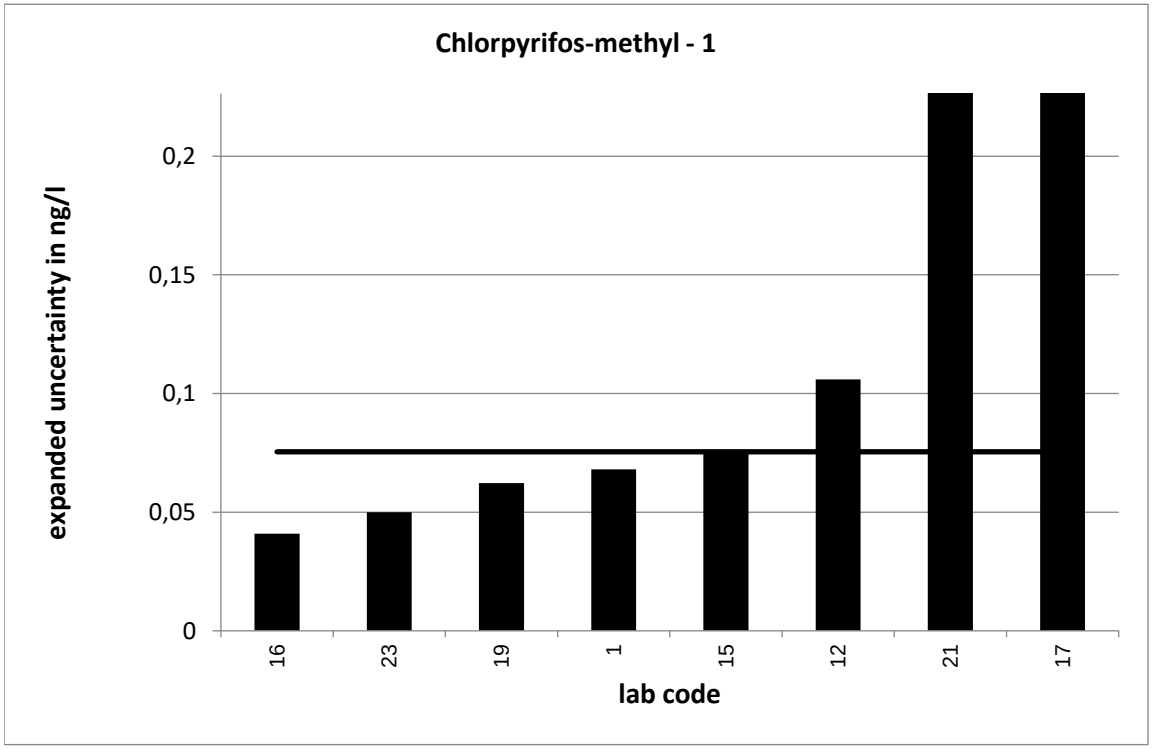
** s = satisfactory, q = questionable, u = unsatisfactory



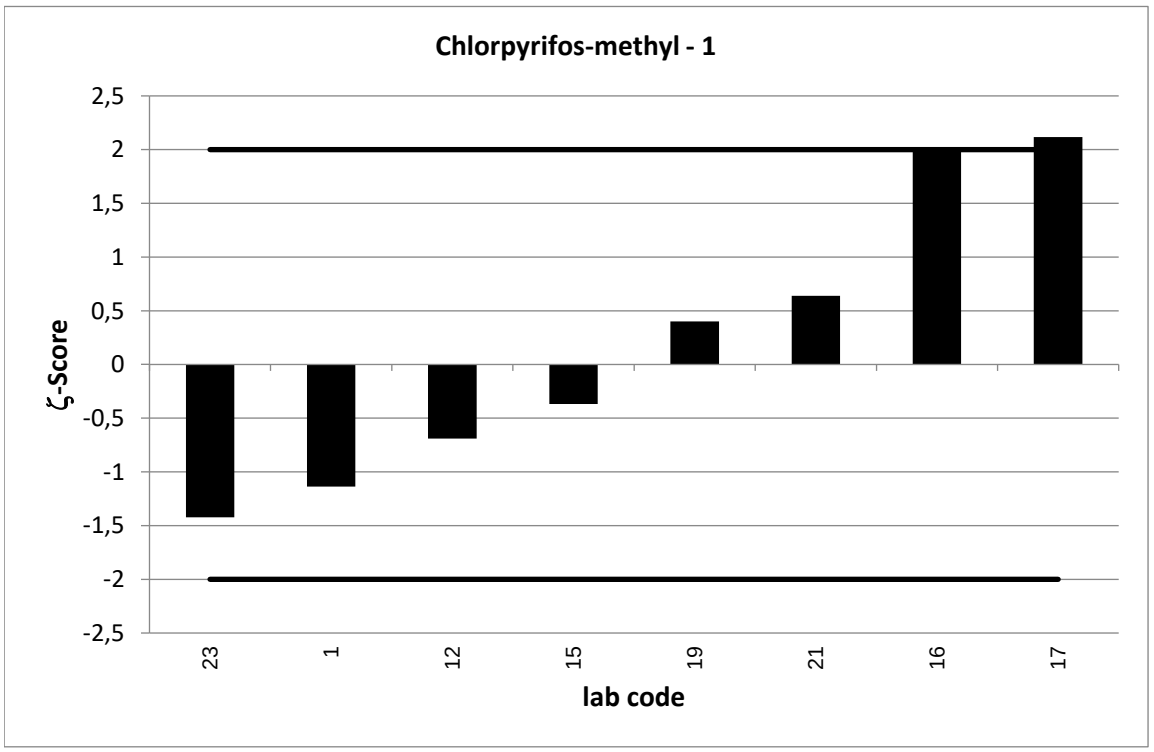
Strongly deviating values are not shown in the diagram.



Strongly deviating values are not correctly shown in the diagram.



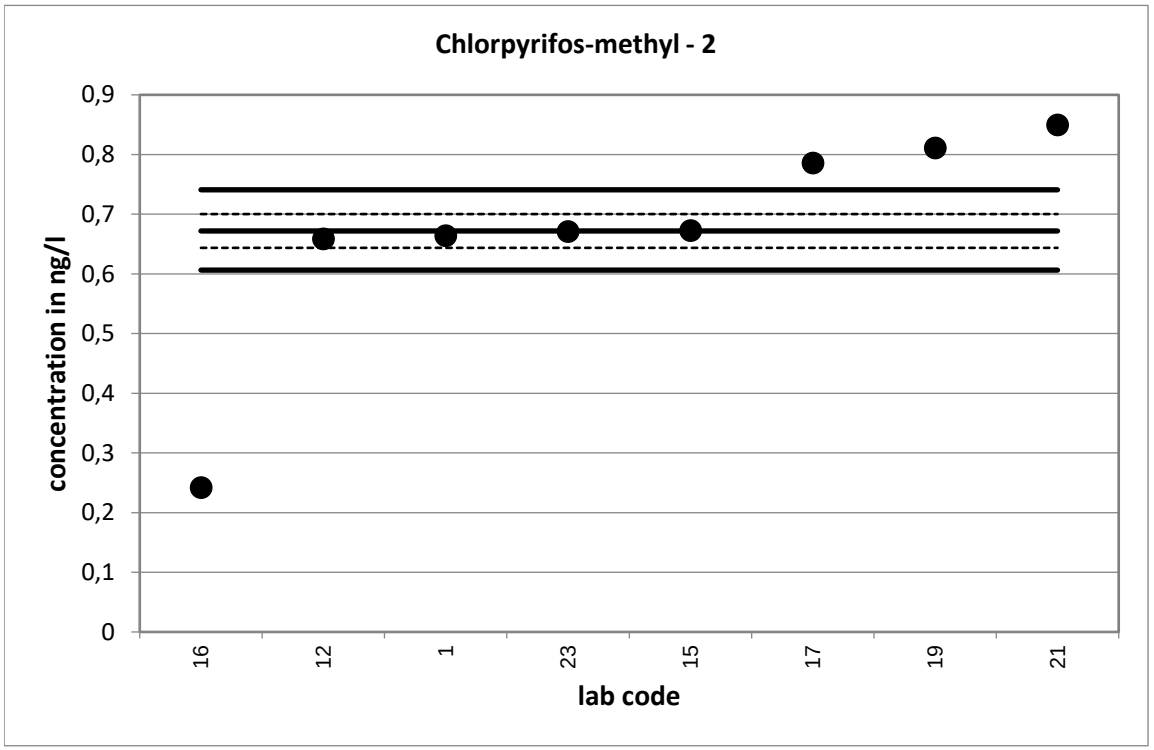
Strongly deviating values are not correctly shown in the diagram.

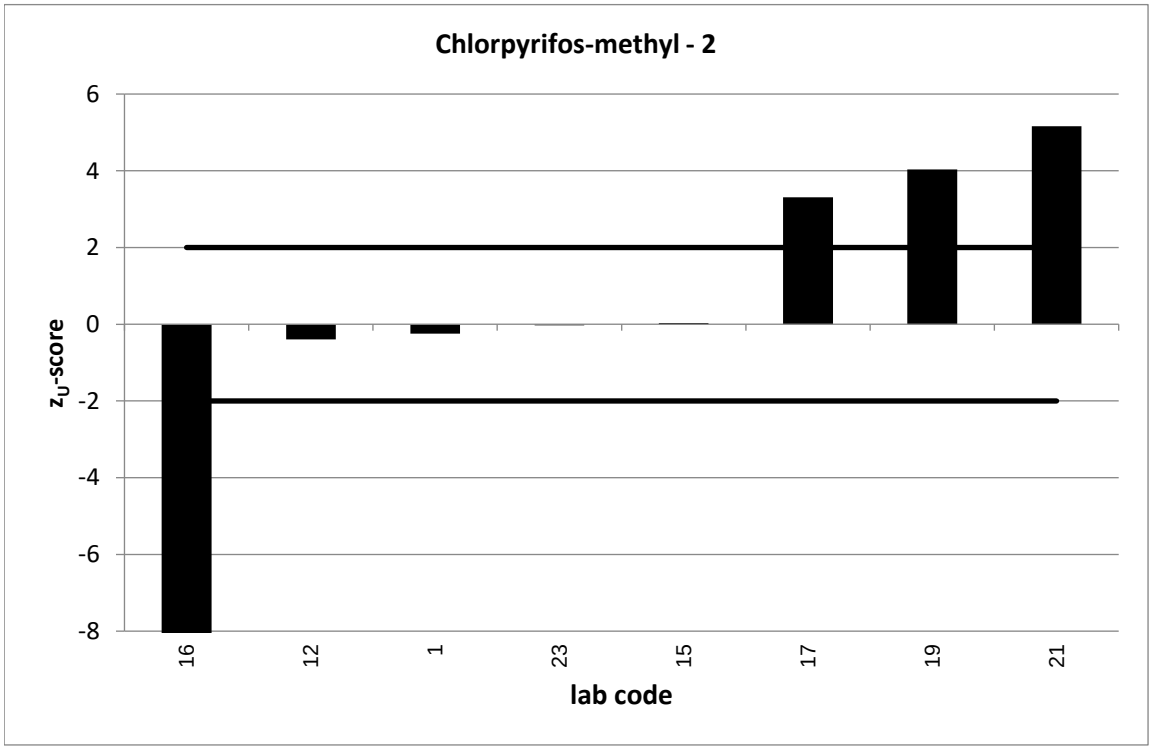


PT 4/24 - Pyrethroids		Chlorpyrifos-methyl - 2			
assigned value [ng/l]*		0,6719	± 0,0283		
upper tolerance limit [ng/l]		0,7409			
lower tolerance limit [ng/l]		0,6063			
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,664	0,133	-0,1	-0,2	s
12	0,659	0,198	-0,1	-0,4	s
15	0,673	0,135	0,0	0,0	s
16	0,242	0,02	-24,8	-13,1	u
17	0,786	0,551	0,4	3,3	u
19	0,811	0,122	2,2	4,0	u
21	0,85	0,425	0,8	5,2	u
23	0,671	0,101	0,0	0,0	s

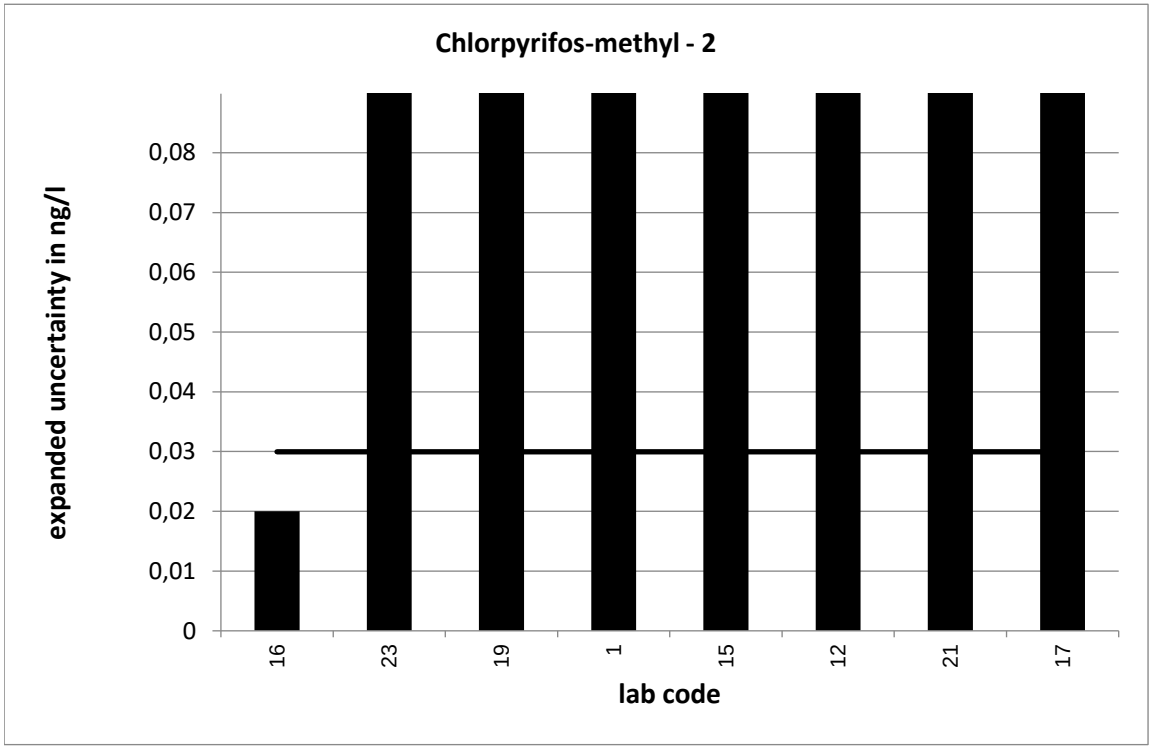
* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

** s = satisfactory, q = questionable, u = unsatisfactory

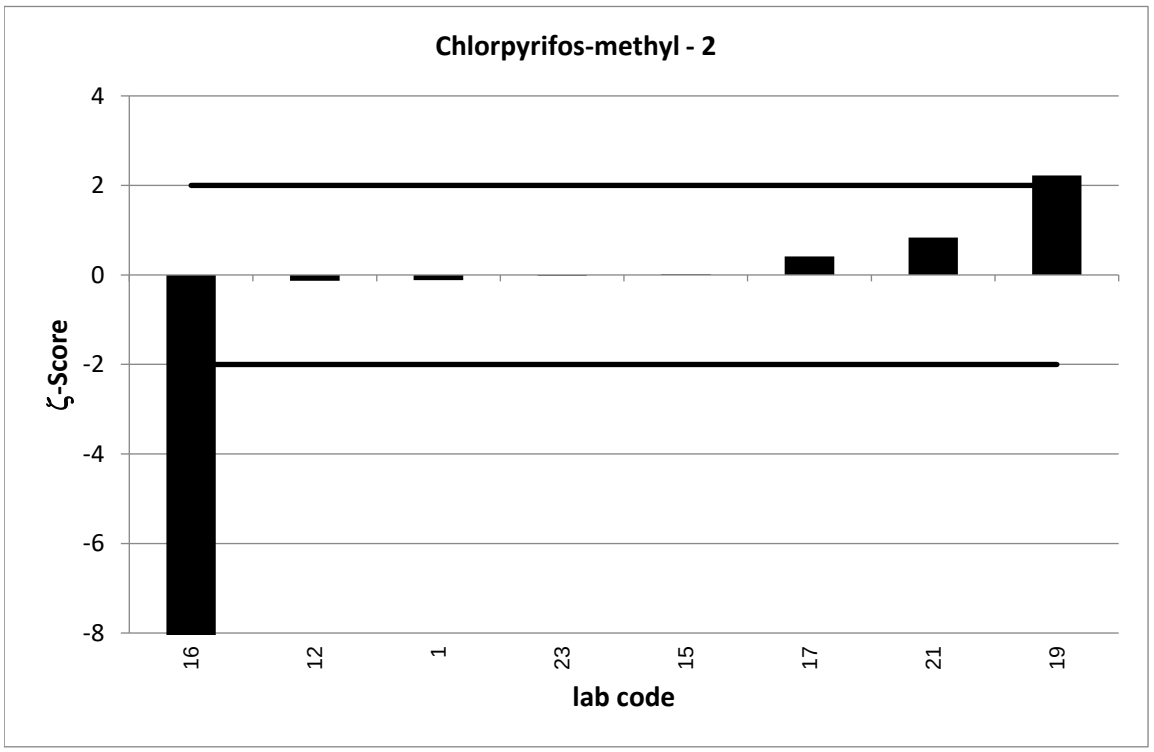




Strongly deviating values are not correctly shown in the diagram.



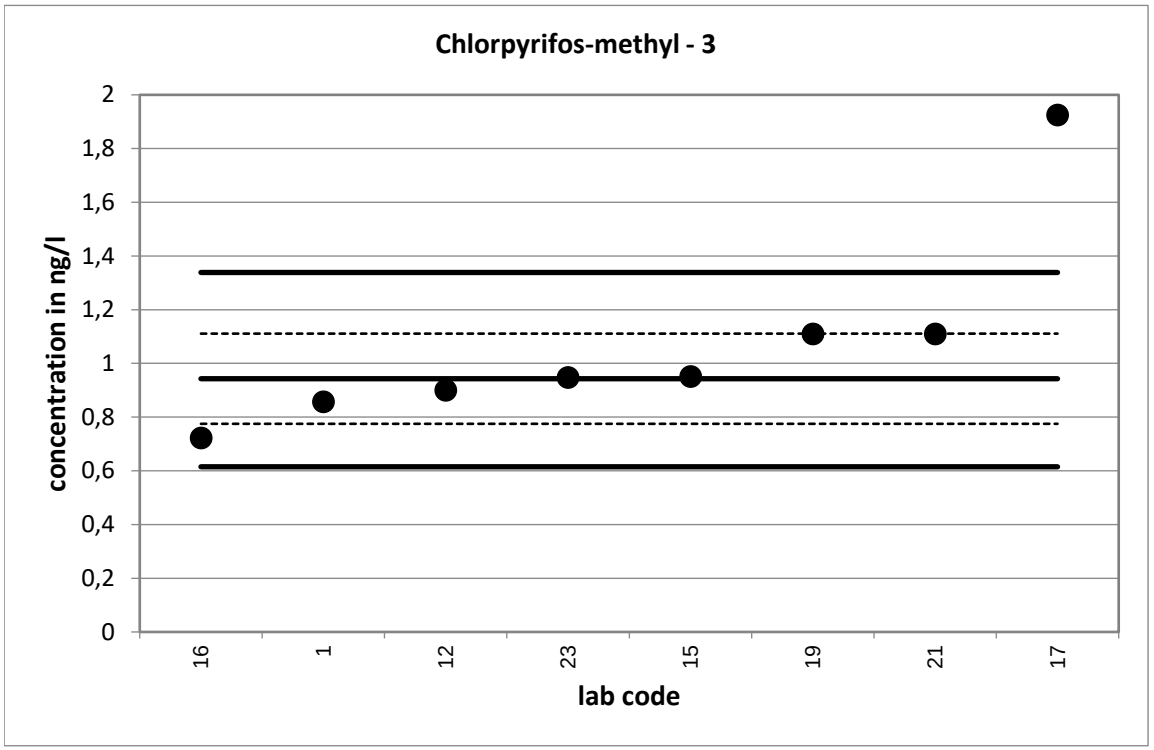
Strongly deviating values are not correctly shown in the diagram.



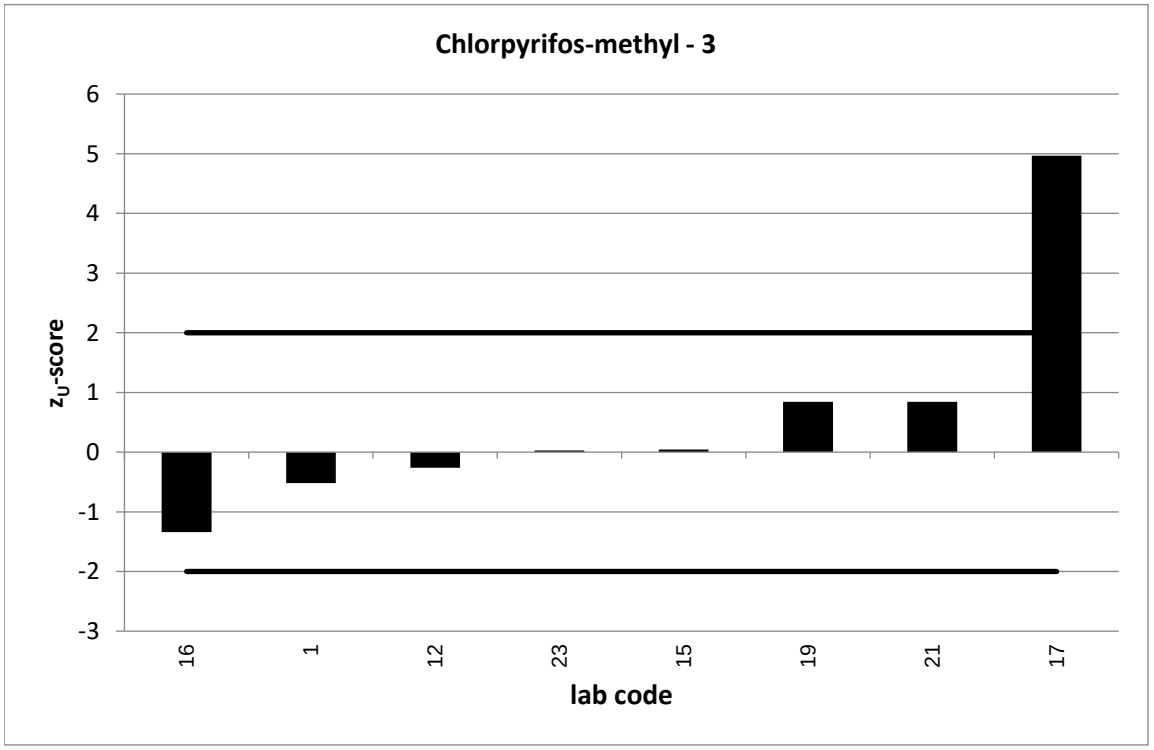
Strongly deviating values are not correctly shown in the diagram.

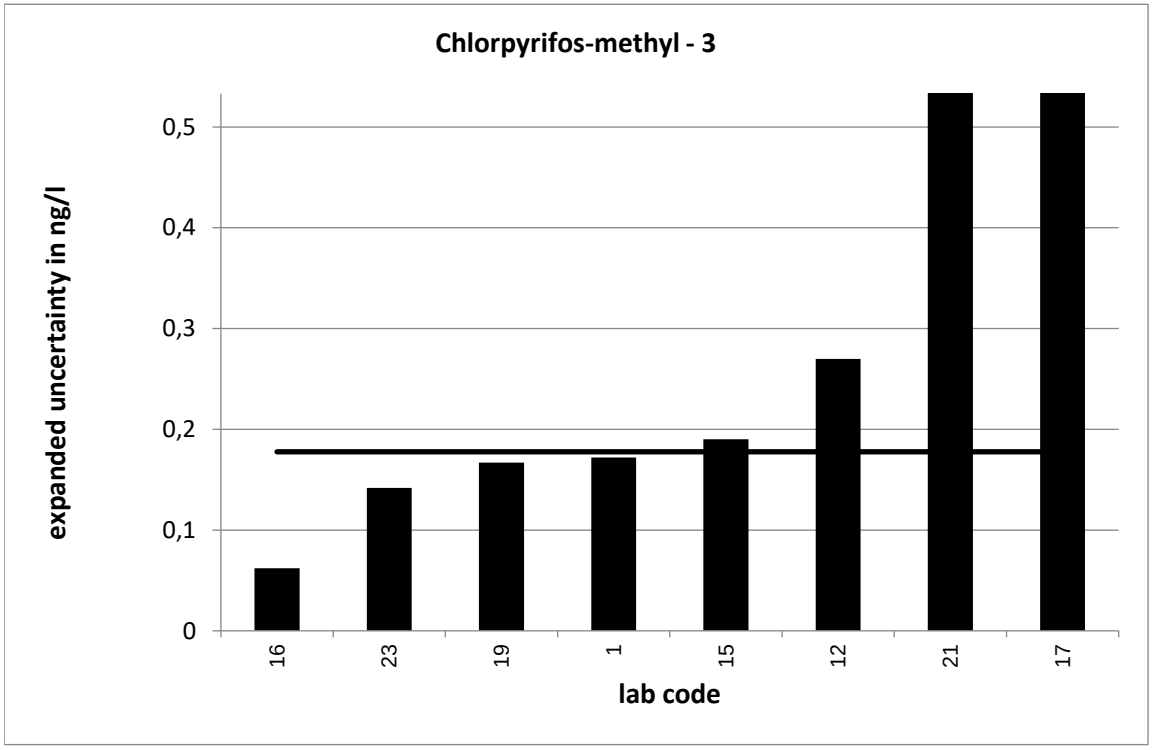
PT 4/24 - Pyrethroids		Chlorpyrifos-methyl - 3			
assigned value [ng/l]*		0,943	± 0,1679		
upper tolerance limit [ng/l]		1,339			
lower tolerance limit [ng/l]		0,6151			
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,858	0,172	-0,7	-0,5	s
12	0,9	0,27	-0,3	-0,3	s
15	0,952	0,19	0,1	0,0	s
16	0,723	0,062	-2,5	-1,3	s
17	1,926	1,348	1,4	5,0	u
19	1,11	0,167	1,4	0,8	s
21	1,11	0,555	0,6	0,8	s
23	0,948	0,142	0,0	0,0	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%
** s = satisfactory, q = questionable, u = unsatisfactory

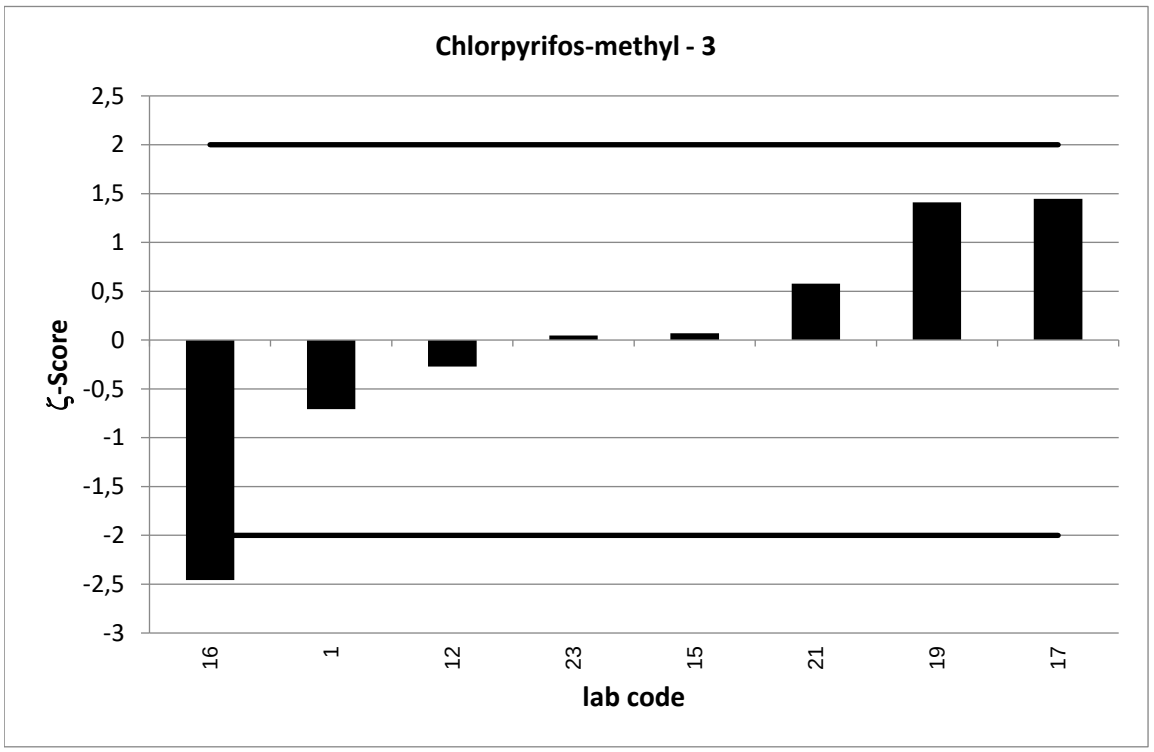


Strongly deviating values are not shown in the diagram.





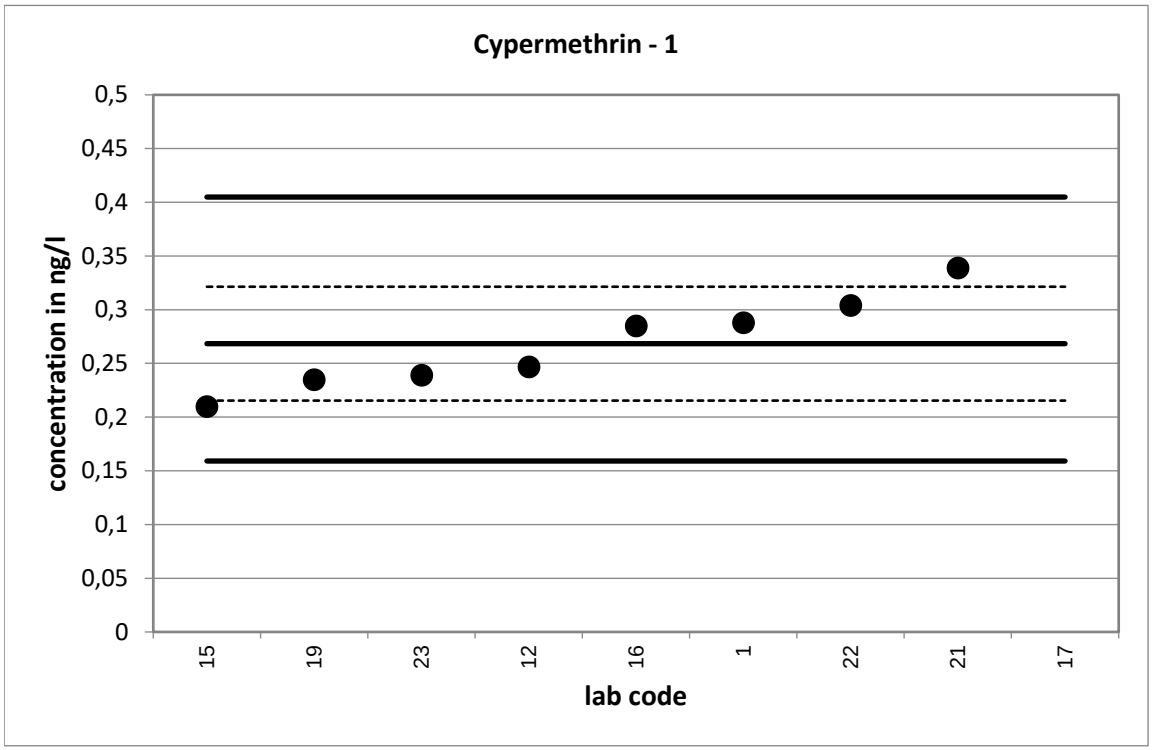
Strongly deviating values are not correctly shown in the diagram.



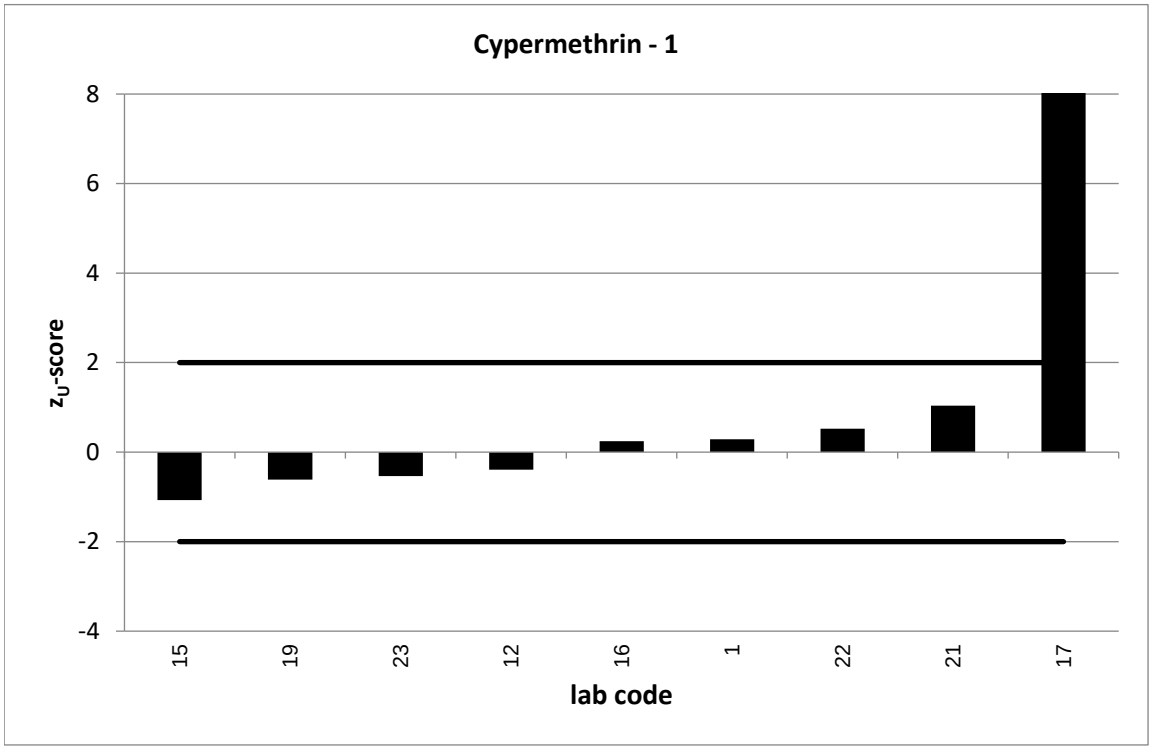
PT 4/24 - Pyrethroids		Cypermethrin - 1			
assigned value [ng/l]*		0,2684	± 0,053		
upper tolerance limit [ng/l]		0,4048			
lower tolerance limit [ng/l]		0,1591			
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,288	0,086	0,4	0,3	s
12	0,247	0,074	-0,5	-0,4	s
15	0,21	0,525	-0,2	-1,1	s
16	0,285	0,031	0,5	0,2	s
17	2,907	2,035	2,6	38,7	u
19	0,235	0,035	-1,0	-0,6	s
21	0,339	0,17	0,8	1,0	s
22	0,304	0,052	1,0	0,5	s
23	0,239	0,048	-0,8	-0,5	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

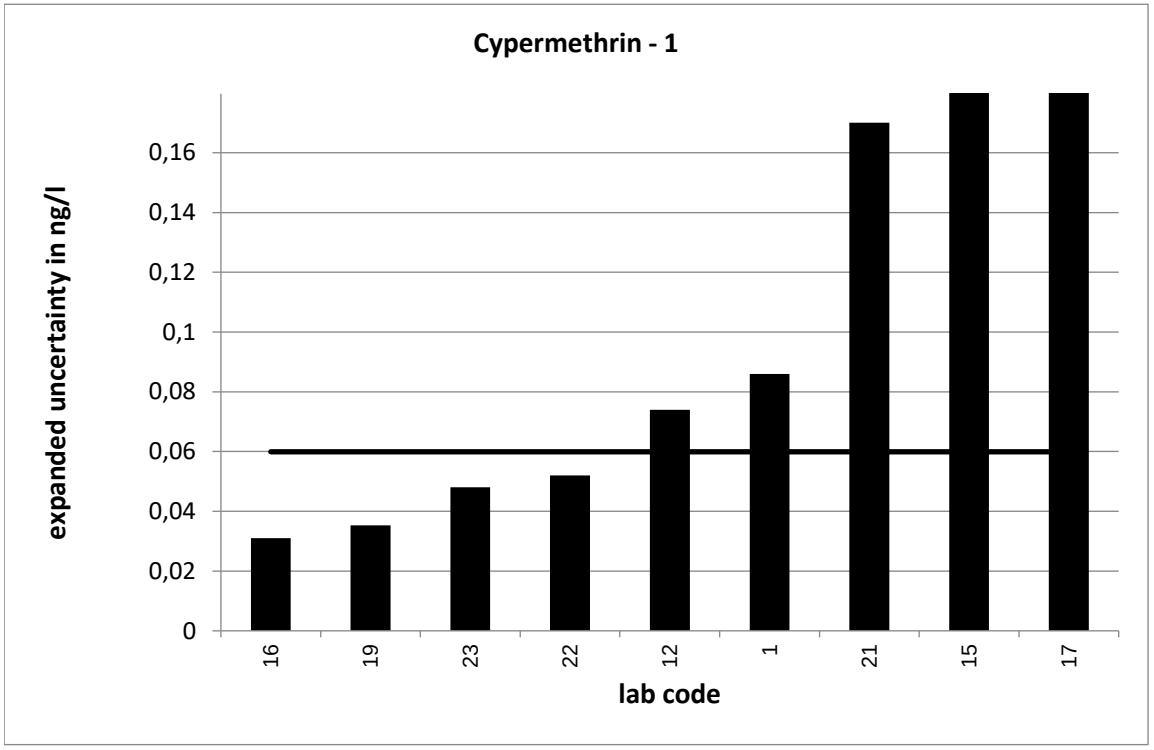
** s = satisfactory, q = questionable, u = unsatisfactory



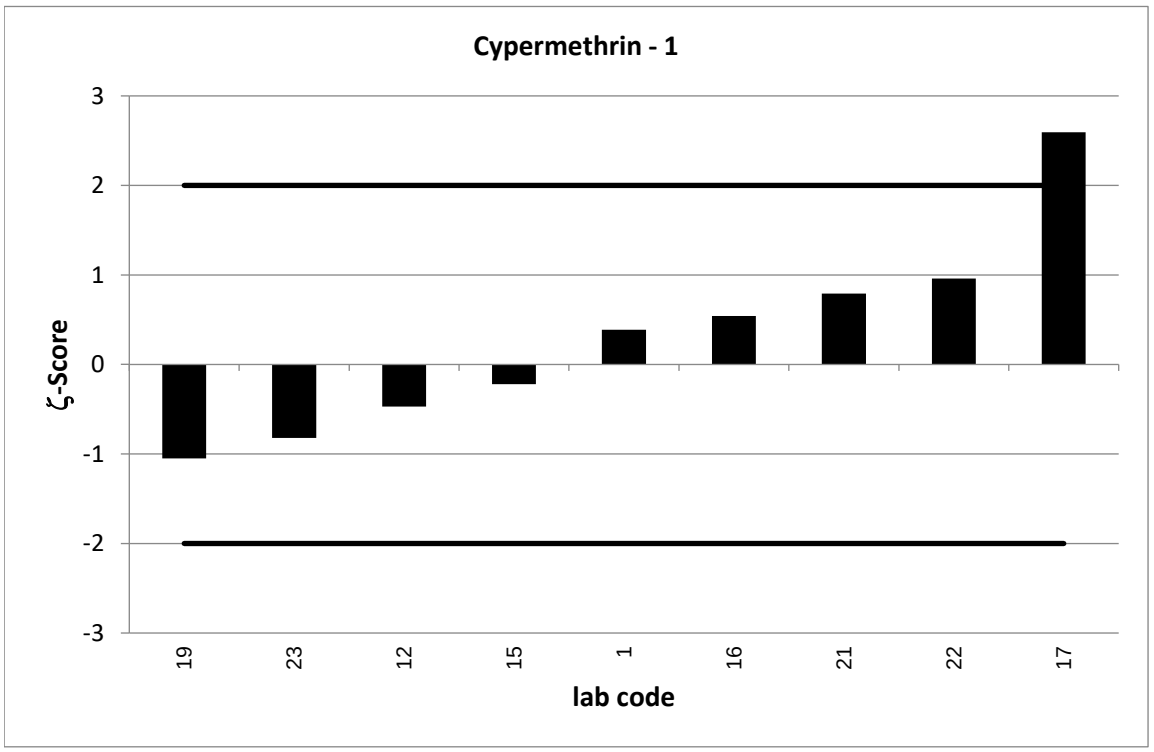
Strongly deviating values are not shown in the diagram.



Strongly deviating values are not correctly shown in the diagram.



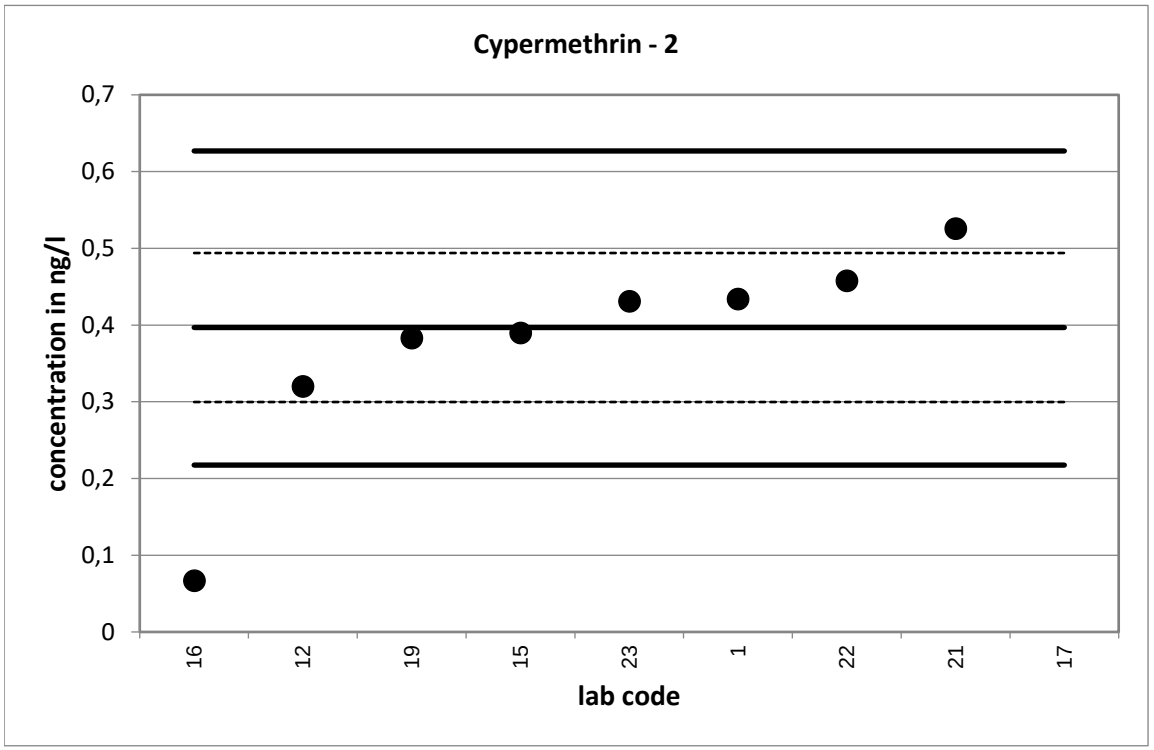
Strongly deviating values are not correctly shown in the diagram.



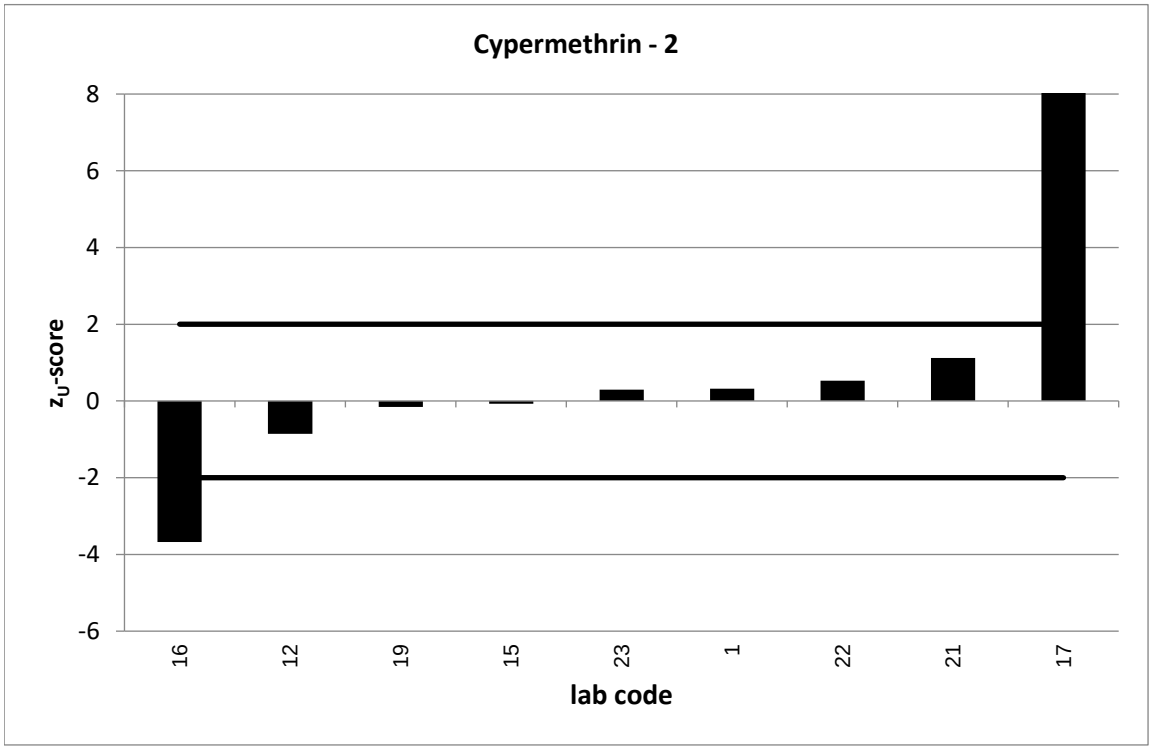
PT 4/24 - Pyrethroids		Cypermethrin - 2			
assigned value [ng/l]*		0,3968	± 0,0971		
upper tolerance limit [ng/l]		0,6269			
lower tolerance limit [ng/l]		0,2175			
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,434	0,13	0,5	0,3	s
12	0,32	0,096	-1,1	-0,9	s
15	0,39	0,098	-0,1	-0,1	s
16	0,067	0,007	-6,8	-3,7	u
17	2,688	1,882	2,4	19,9	u
19	0,383	0,058	-0,2	-0,2	s
21	0,526	0,263	0,9	1,1	s
22	0,458	0,078	1,0	0,5	s
23	0,431	0,086	0,5	0,3	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

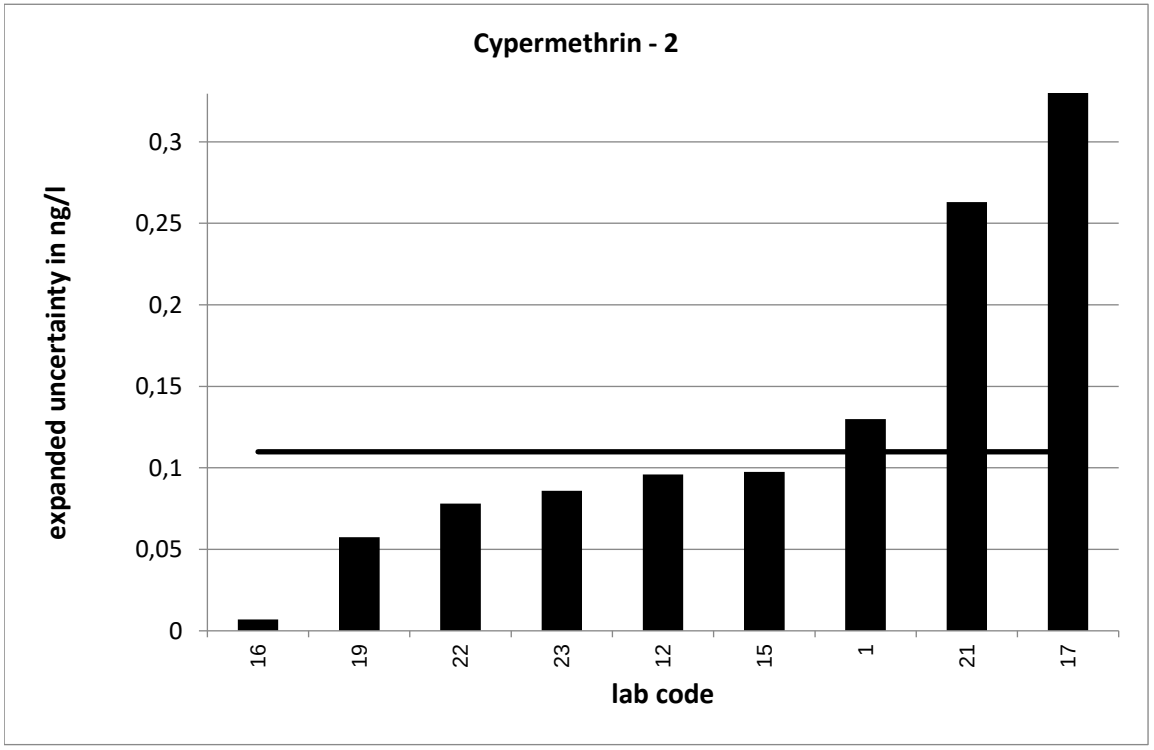
** s = satisfactory, q = questionable, u = unsatisfactory



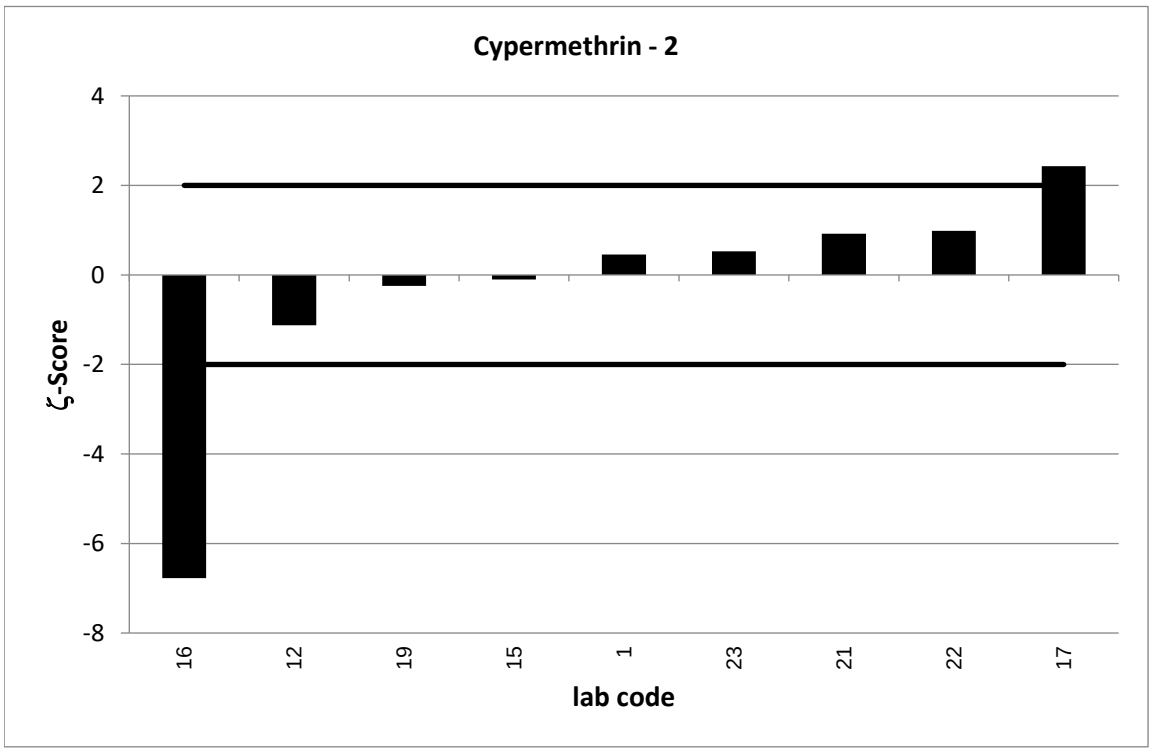
Strongly deviating values are not shown in the diagram.



Strongly deviating values are not correctly shown in the diagram.



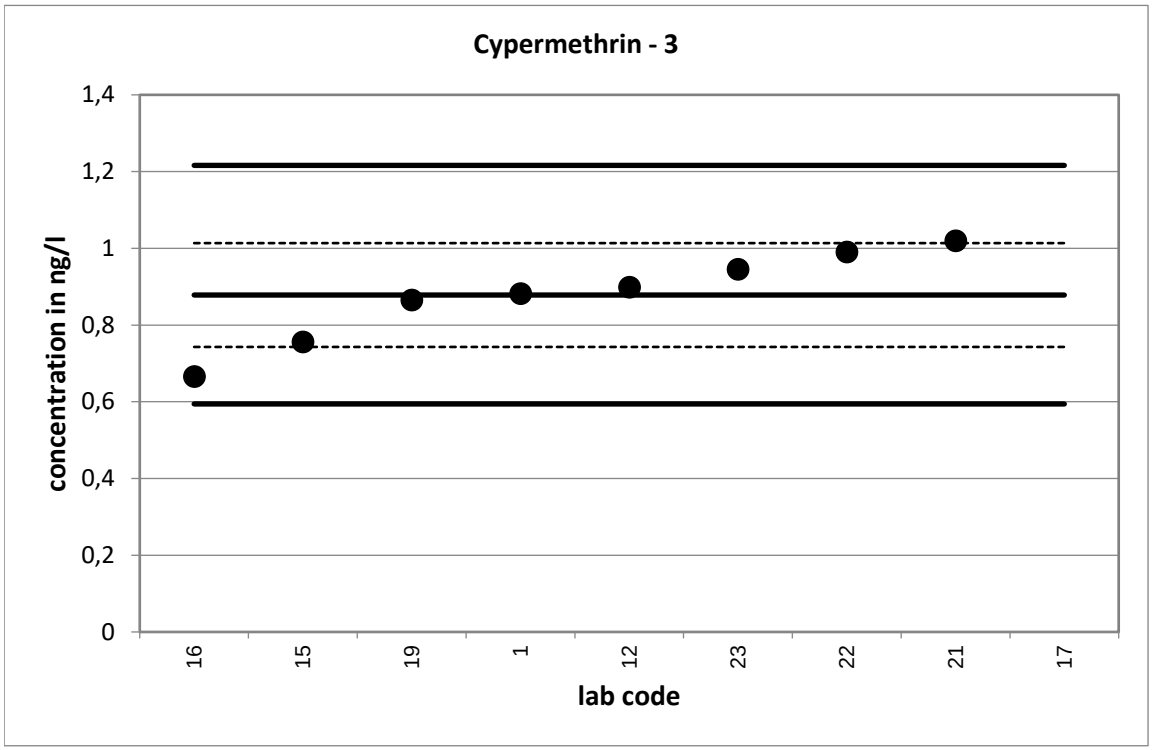
Strongly deviating values are not correctly shown in the diagram.



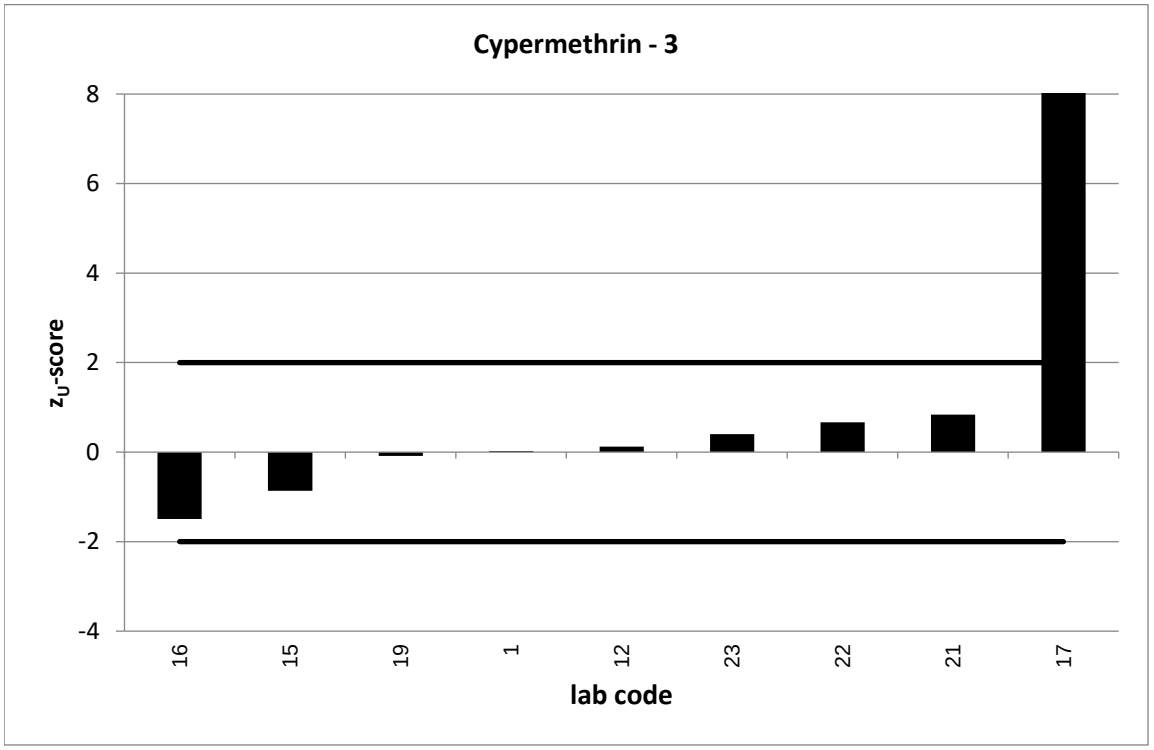
PT 4/24 - Pyrethroids		Cypermethrin - 3			
assigned value [ng/l]*		0,8783	± 0,1353		
upper tolerance limit [ng/l]		1,216			
lower tolerance limit [ng/l]		0,5943			
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,882	0,265	0,0	0,0	s
12	0,899	0,27	0,1	0,1	s
15	0,756	0,189	-1,1	-0,9	s
16	0,666	0,072	-2,8	-1,5	s
17	5,09	3,563	2,4	24,9	u
19	0,866	0,13	-0,1	-0,1	s
21	1,02	0,512	0,5	0,8	s
22	0,991	0,168	1,0	0,7	s
23	0,946	0,189	0,6	0,4	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

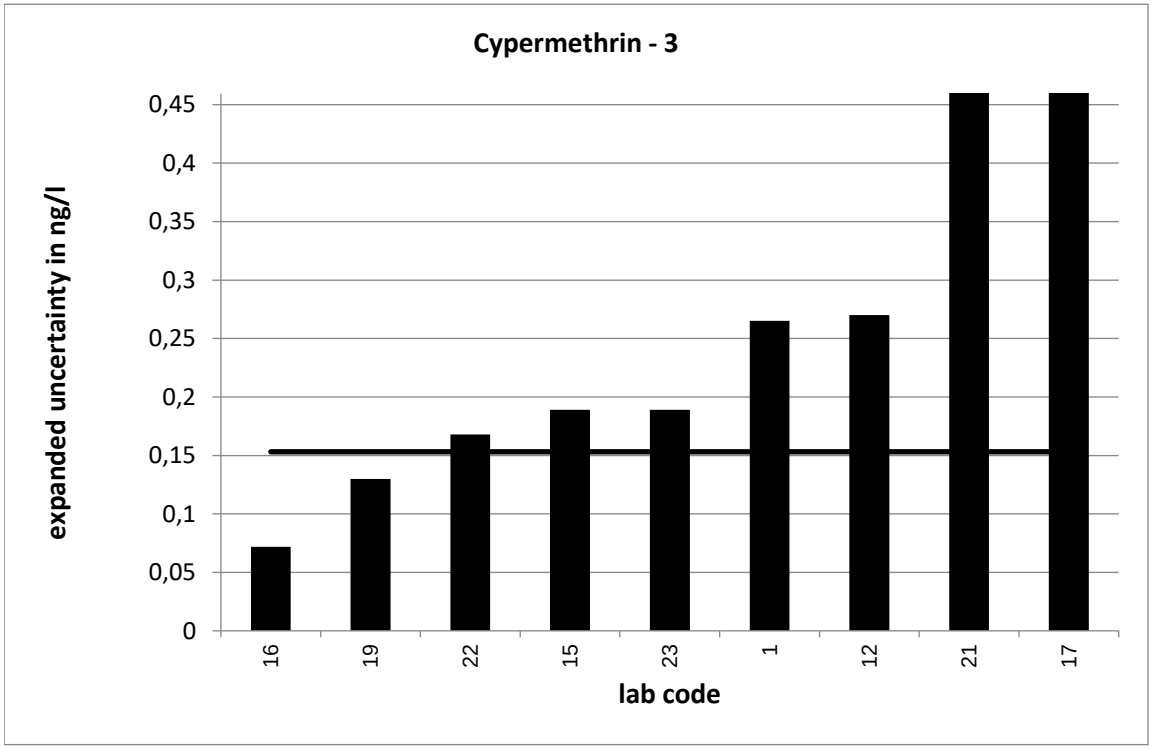
** s = satisfactory, q = questionable, u = unsatisfactory



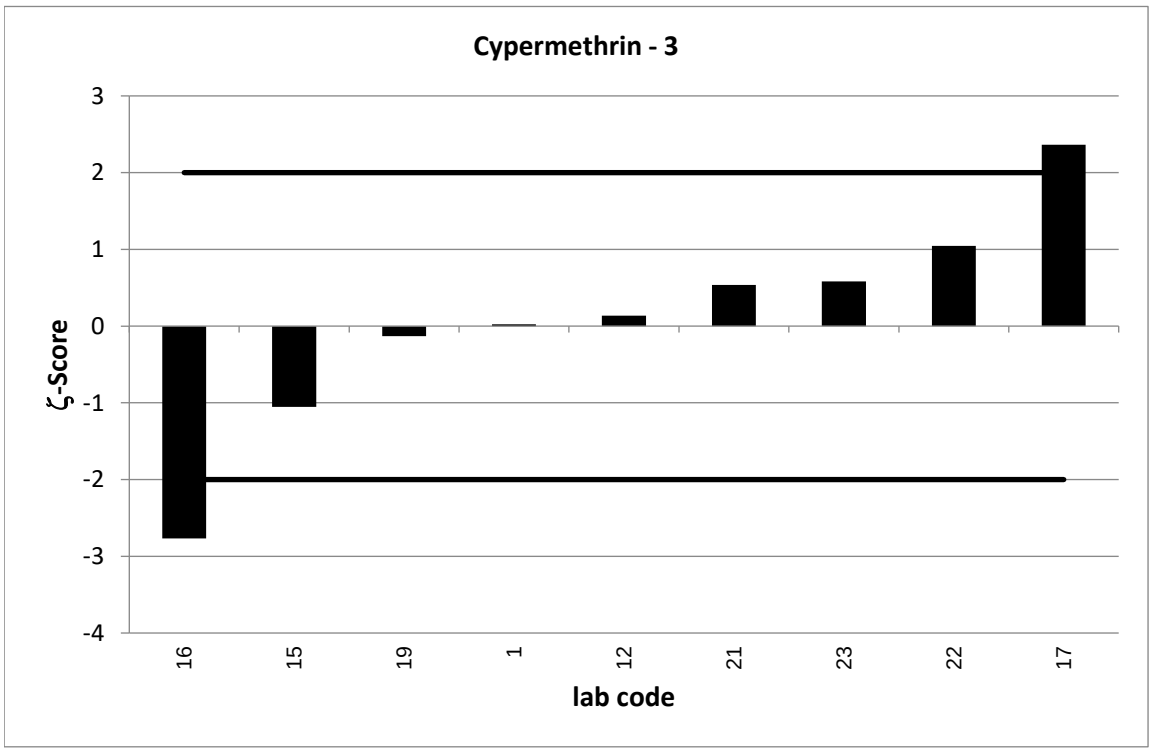
Strongly deviating values are not shown in the diagram.



Strongly deviating values are not correctly shown in the diagram.



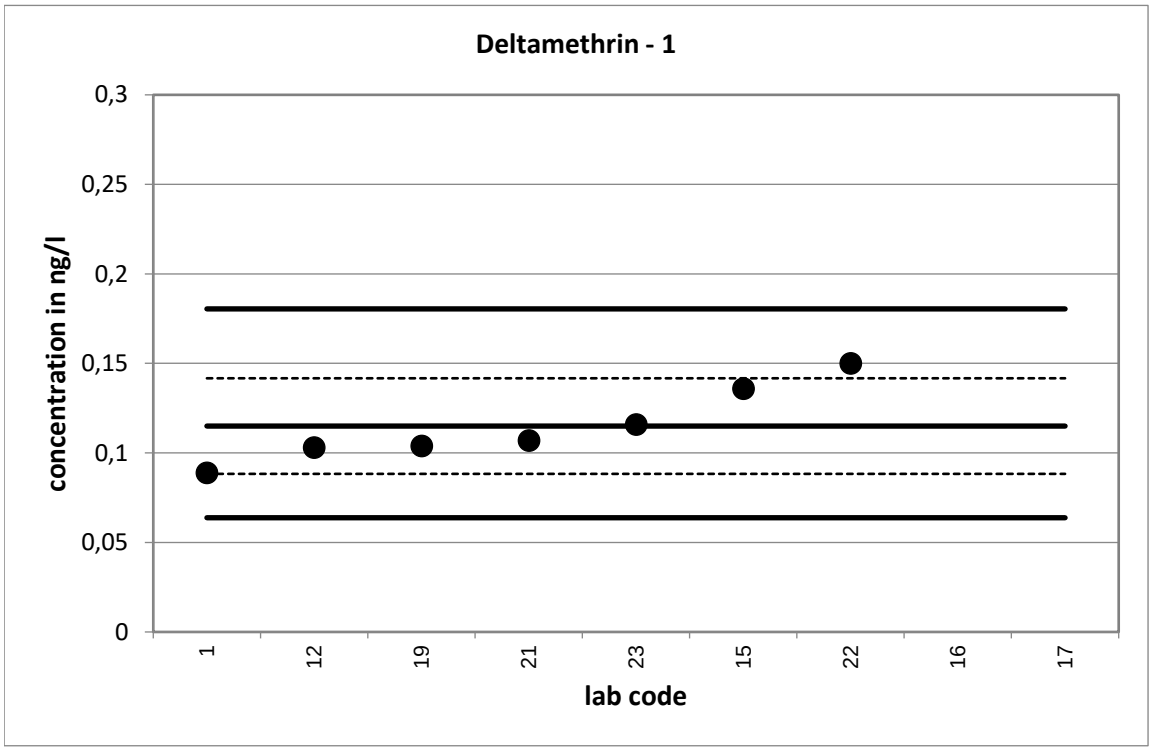
Strongly deviating values are not correctly shown in the diagram.



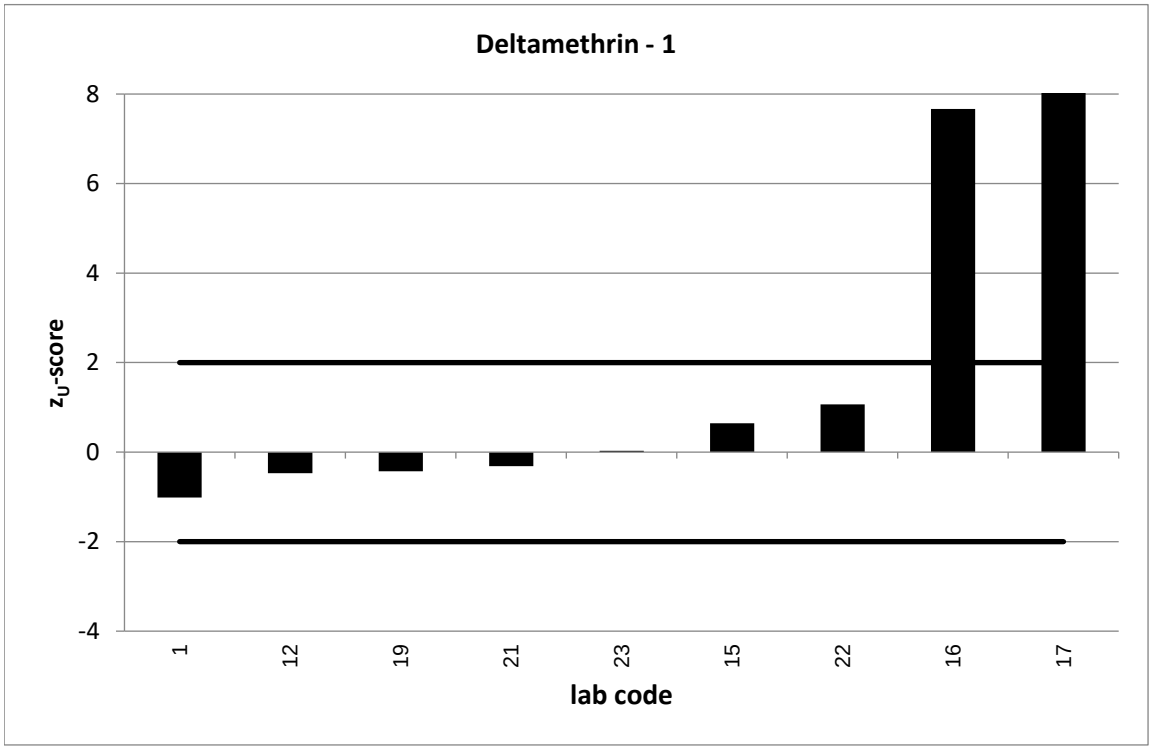
PT 4/24 - Pyrethroids		Deltamethrin - 1			
assigned value [ng/l]*			0,115	± 0,0267	
upper tolerance limit [ng/l]			0,1804		
lower tolerance limit [ng/l]			0,06379		
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,089	0,027	-1,4	-1,0	s
12	0,103	0,031	-0,6	-0,5	s
15	0,136	0,027	1,1	0,6	s
16	0,366	0,173	2,9	7,7	u
17	3,61	2,527	2,8	106,8	u
19	0,104	0,016	-0,7	-0,4	s
21	0,107	0,054	-0,3	-0,3	s
22	0,15	0,018	2,2	1,1	s
23	0,116	0,023	0,1	0,0	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

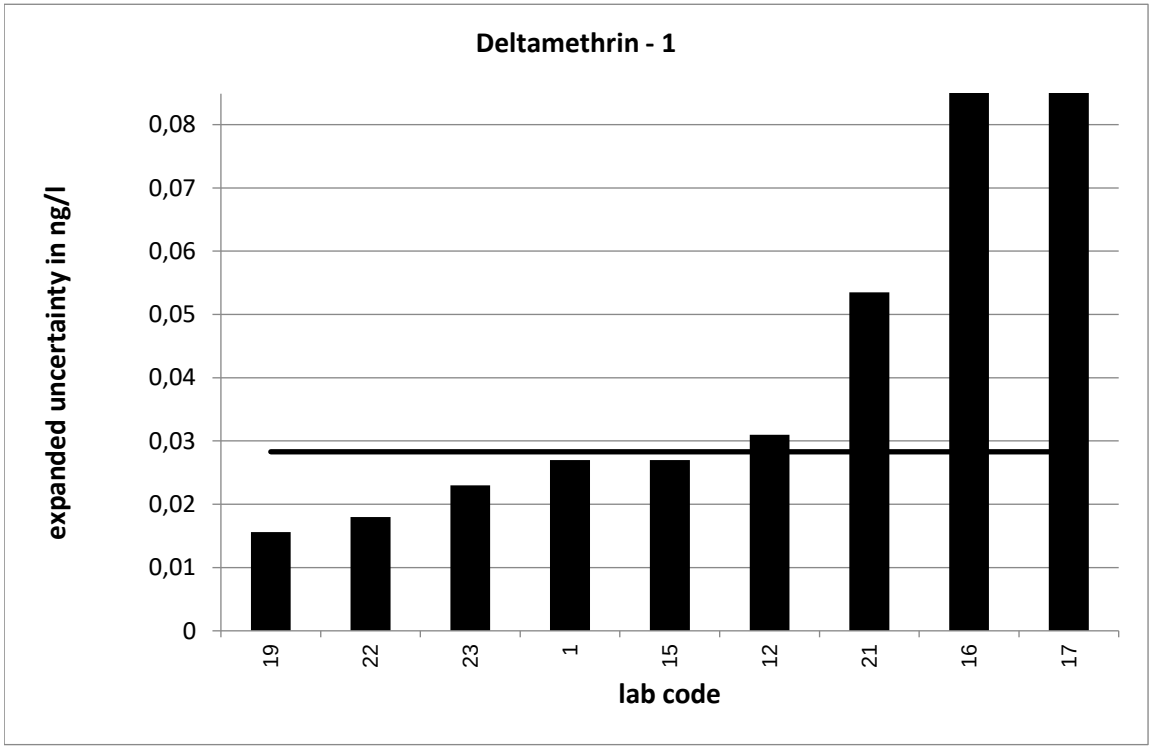
** s = satisfactory, q = questionable, u = unsatisfactory



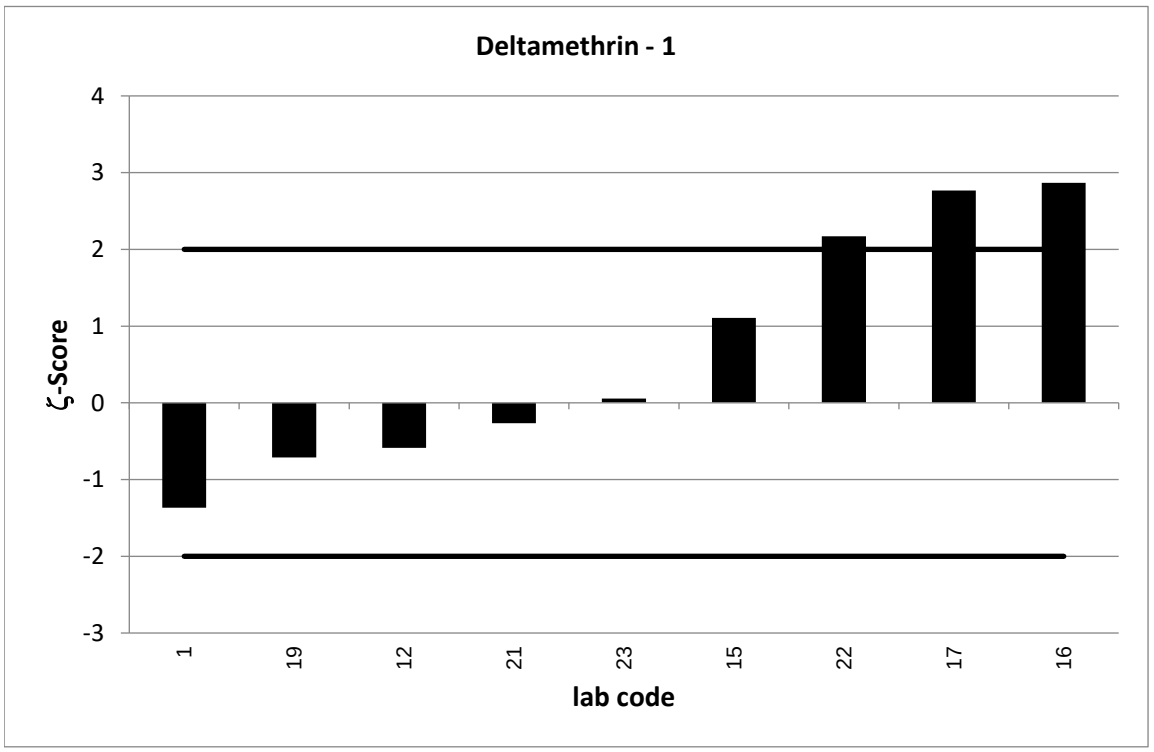
Strongly deviating values are not shown in the diagram.



Strongly deviating values are not correctly shown in the diagram.



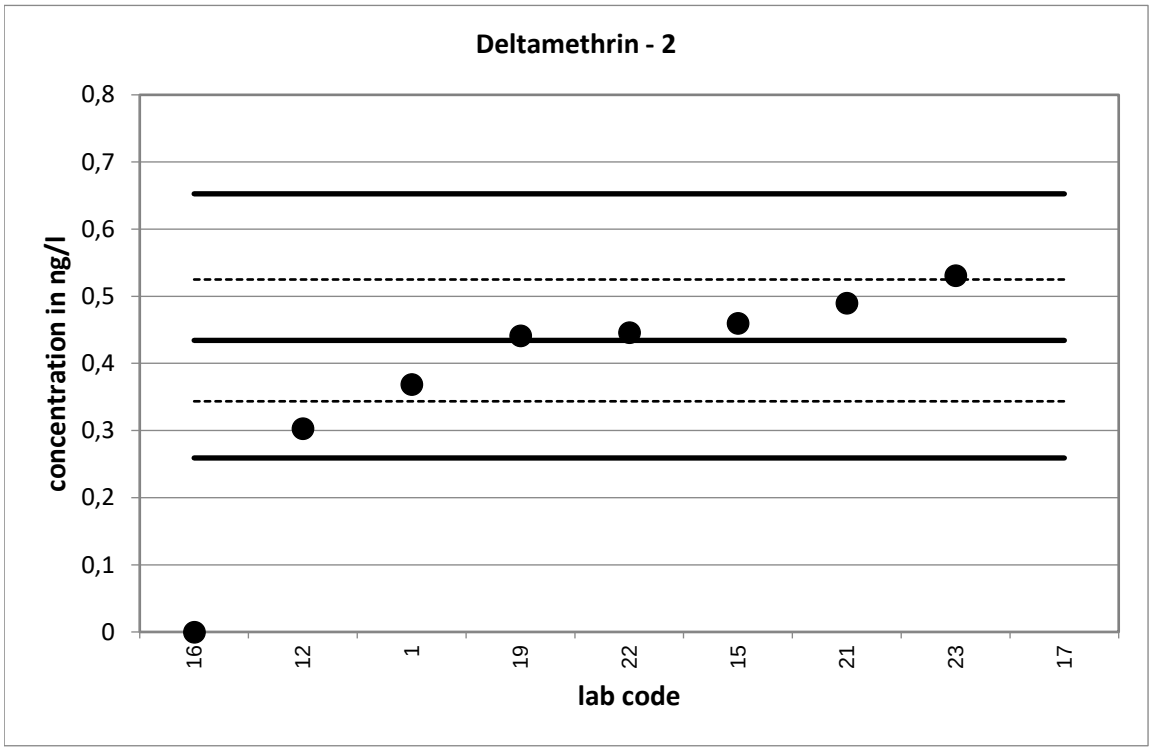
Strongly deviating values are not correctly shown in the diagram.



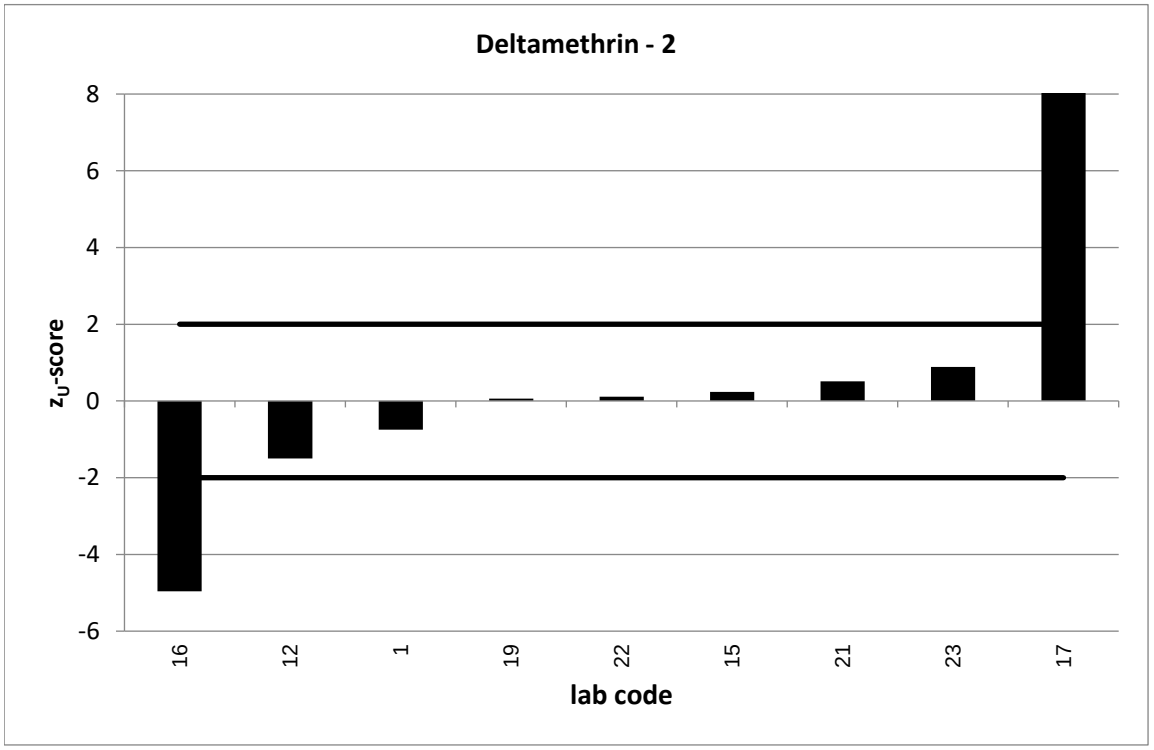
PT 4/24 - Pyrethroids		Deltamethrin - 2			
assigned value [ng/l]*		0,4343	± 0,0907		
upper tolerance limit [ng/l]		0,6526			
lower tolerance limit [ng/l]		0,2592			
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,369	0,111	-0,9	-0,7	s
12	0,303	0,091	-2,0	-1,5	s
15	0,46	0,092	0,4	0,2	s
16	0	0	-9,6	-5,0	u
17	1,913	1,339	2,2	13,5	u
19	0,441	0,066	0,1	0,1	s
21	0,49	0,245	0,4	0,5	s
22	0,446	0,054	0,2	0,1	s
23	0,531	0,106	1,4	0,9	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

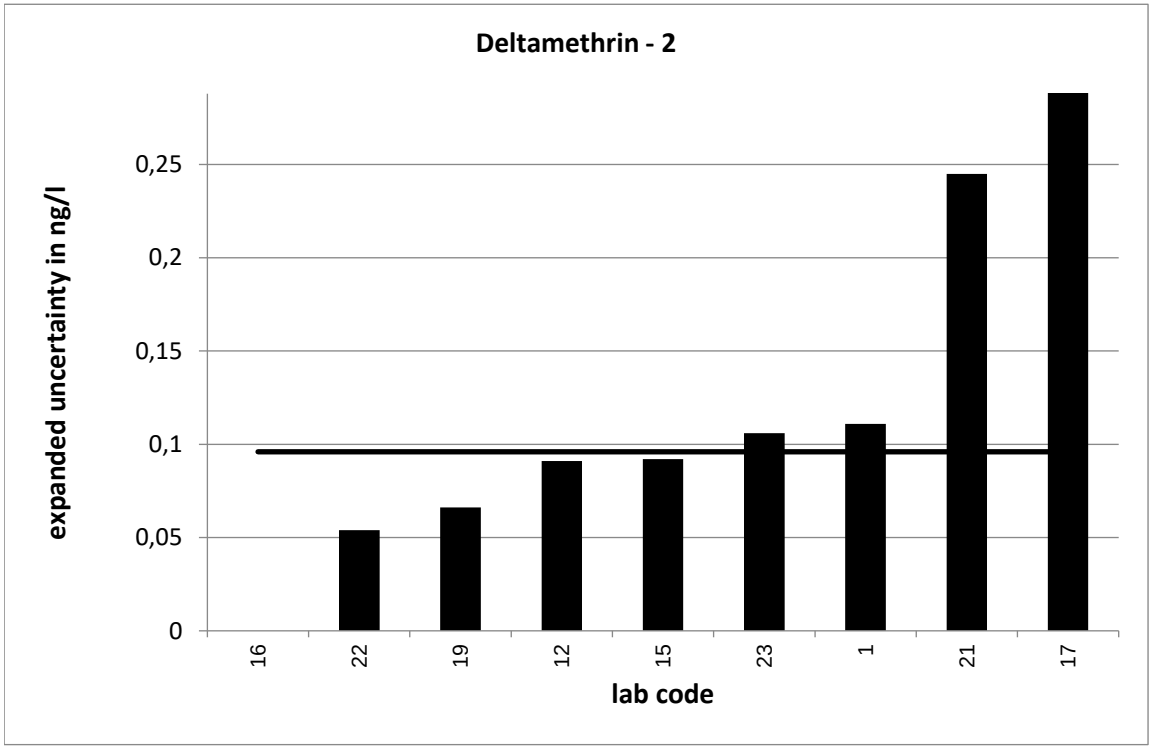
** s = satisfactory, q = questionable, u = unsatisfactory



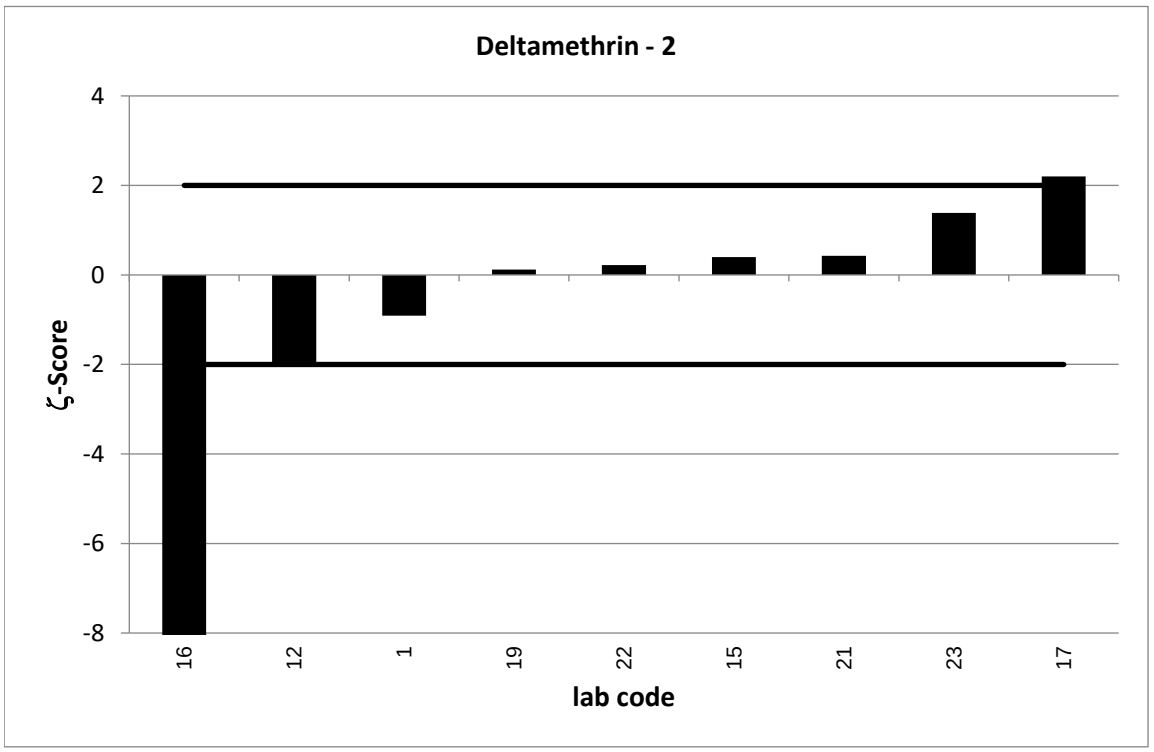
Strongly deviating values are not shown in the diagram.



Strongly deviating values are not correctly shown in the diagram.



Strongly deviating values are not correctly shown in the diagram.

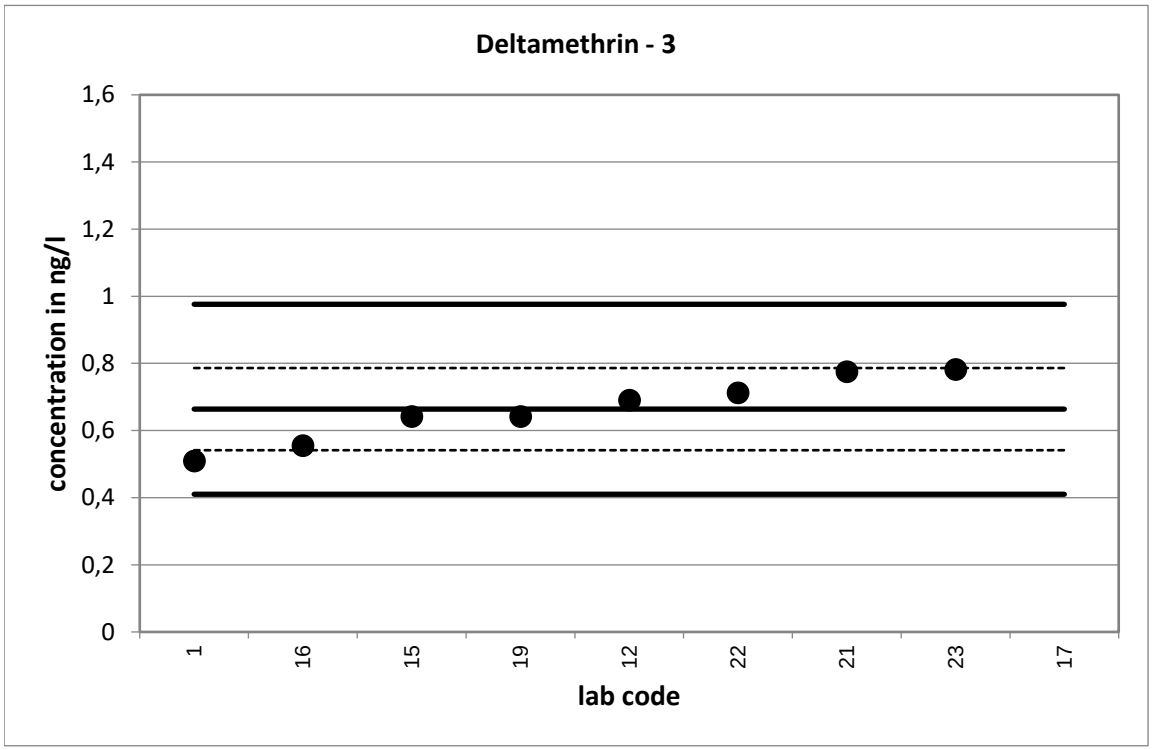


Strongly deviating values are not correctly shown in the diagram.

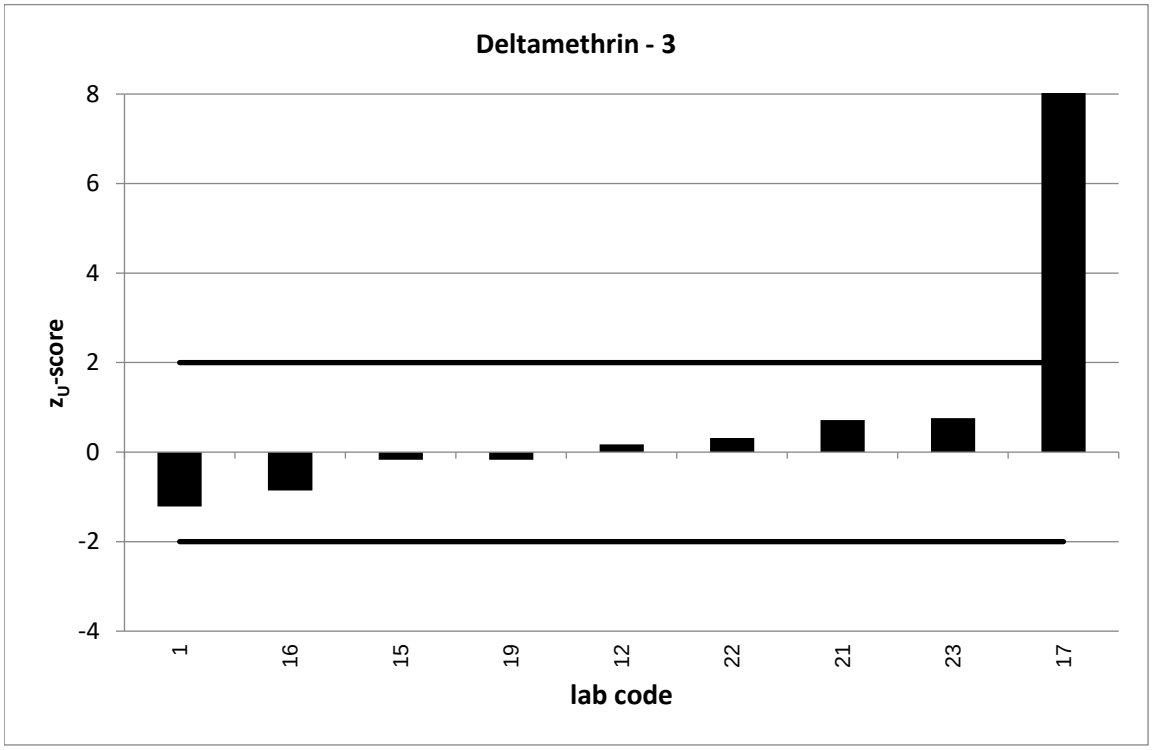
PT 4/24 - Pyrethroids		Deltamethrin - 3			
assigned value [ng/l]*		0,6639	± 0,1224		
upper tolerance limit [ng/l]		0,9761			
lower tolerance limit [ng/l]		0,4102			
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,51	0,153	-1,6	-1,2	s
12	0,691	0,207	0,2	0,2	s
15	0,642	0,128	-0,2	-0,2	s
16	0,555	0,263	-0,8	-0,9	s
17	4,219	2,953	2,4	22,8	u
19	0,642	0,096	-0,3	-0,2	s
21	0,776	0,388	0,6	0,7	s
22	0,713	0,086	0,7	0,3	s
23	0,782	0,156	1,2	0,8	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

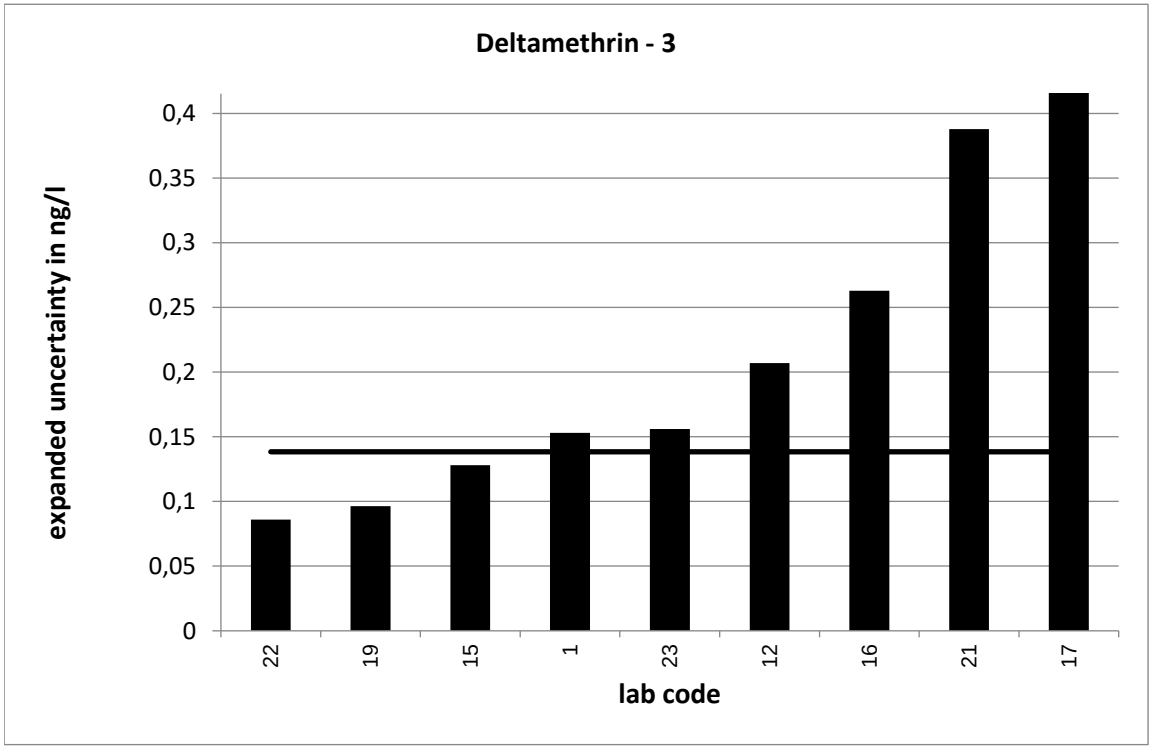
** s = satisfactory, q = questionable, u = unsatisfactory



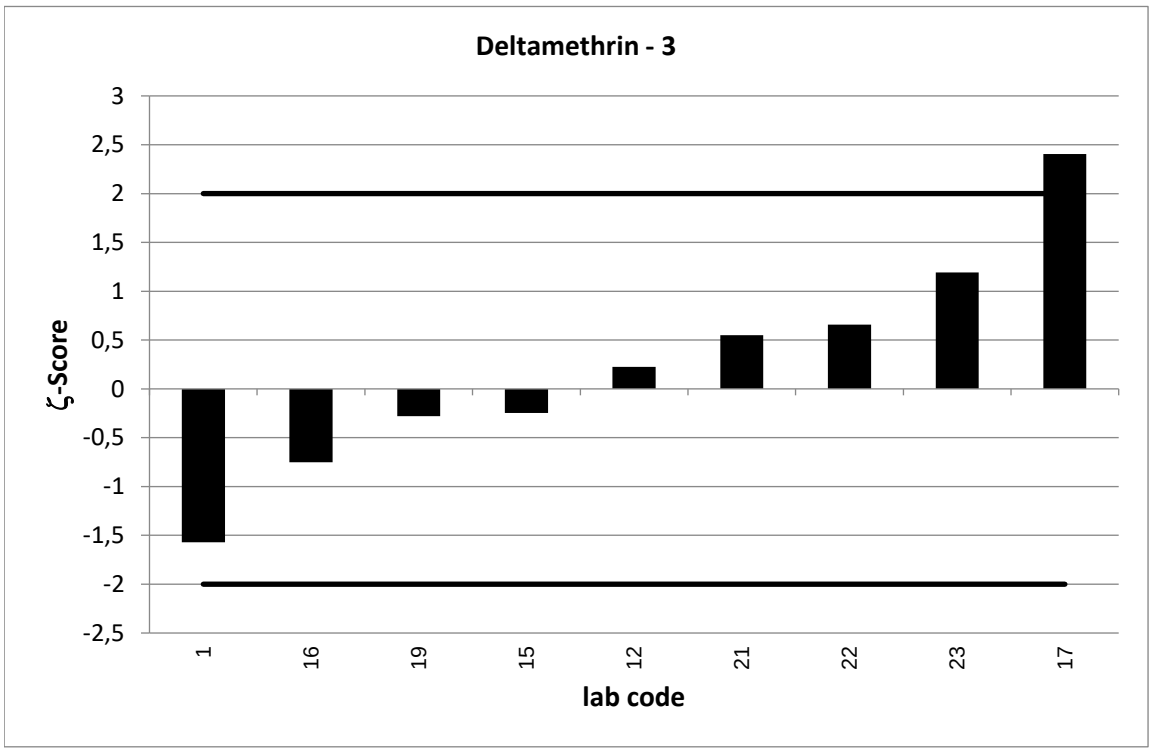
Strongly deviating values are not shown in the diagram.



Strongly deviating values are not correctly shown in the diagram.



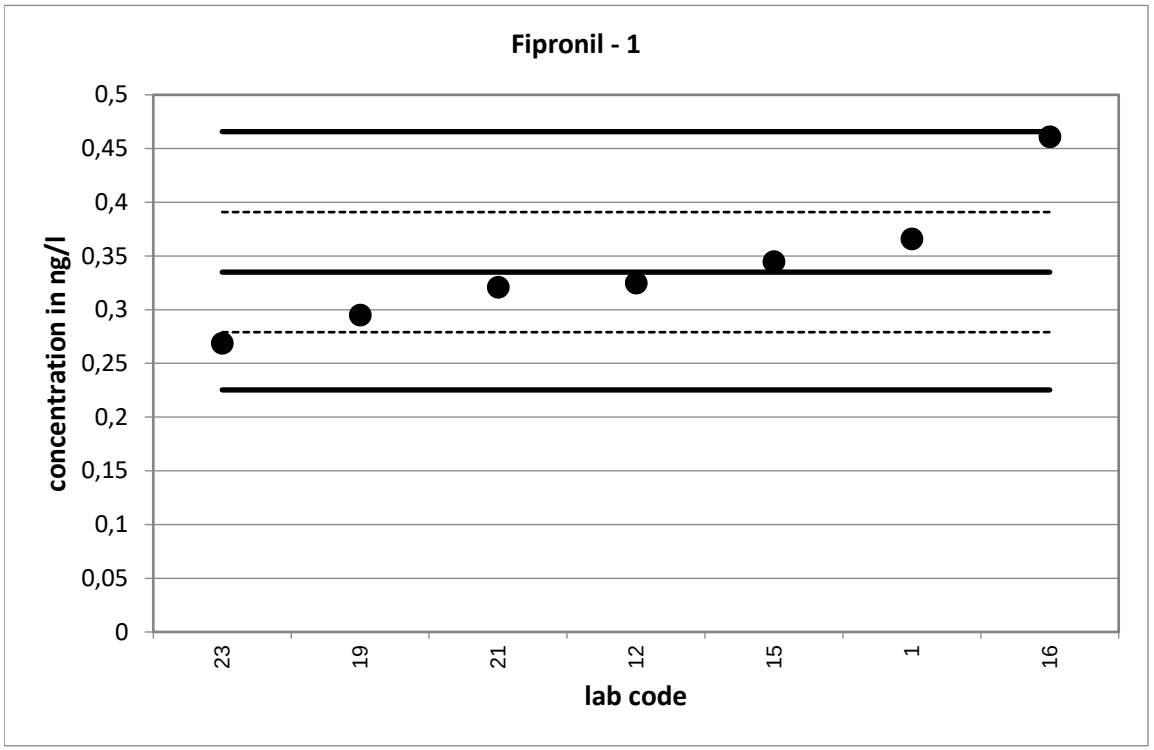
Strongly deviating values are not correctly shown in the diagram.



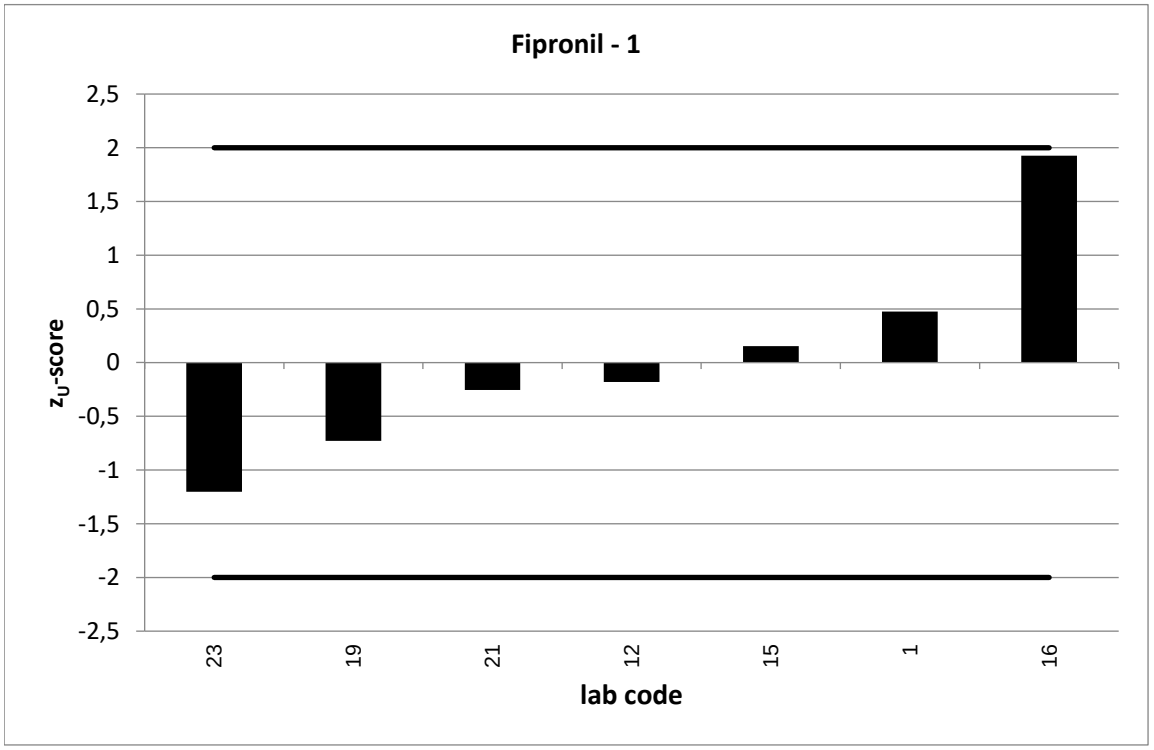
PT 4/24 - Pyrethroids		Fipronil - 1			
assigned value [ng/l]*			0,335	± 0,0559	
upper tolerance limit [ng/l]			0,4657		
lower tolerance limit [ng/l]			0,2253		
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,366	0,11	0,5	0,5	s
12	0,325	0,097	-0,2	-0,2	s
15	0,345	0,104	0,2	0,2	s
16	0,461	0,047	3,5	1,9	s
19	0,295	0,089	-0,8	-0,7	s
21	0,321	0,128	-0,2	-0,3	s
23	0,269	0,067	-1,5	-1,2	s

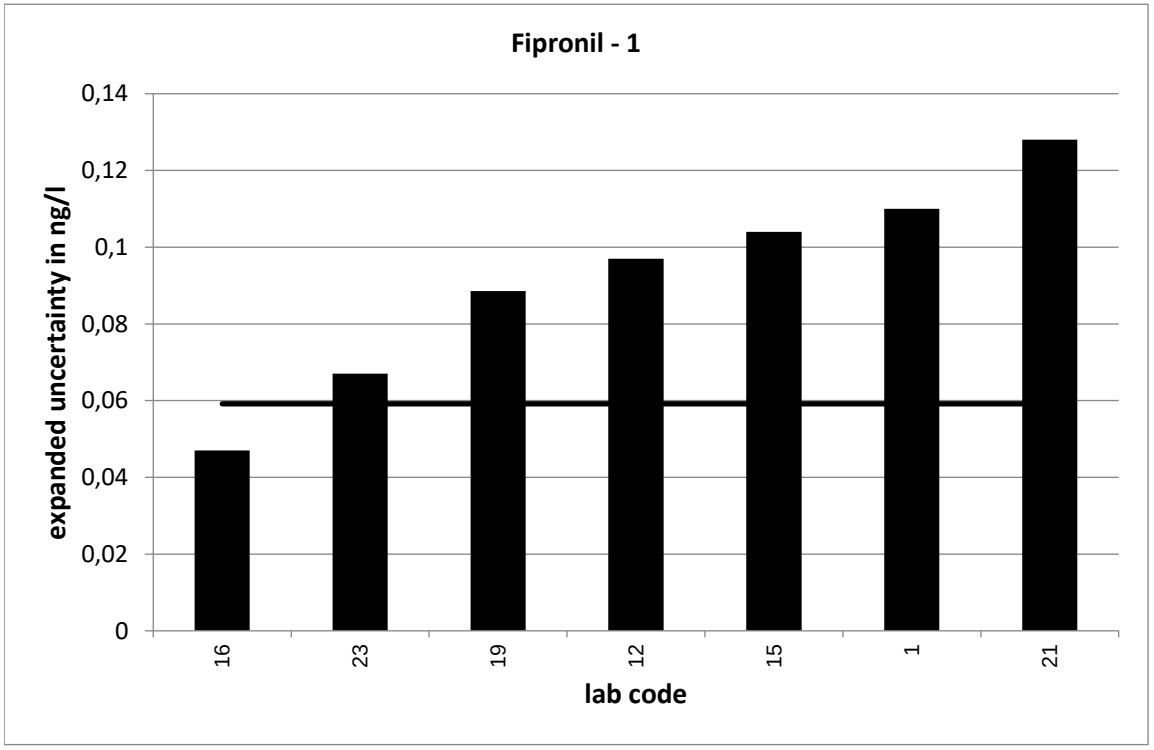
* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

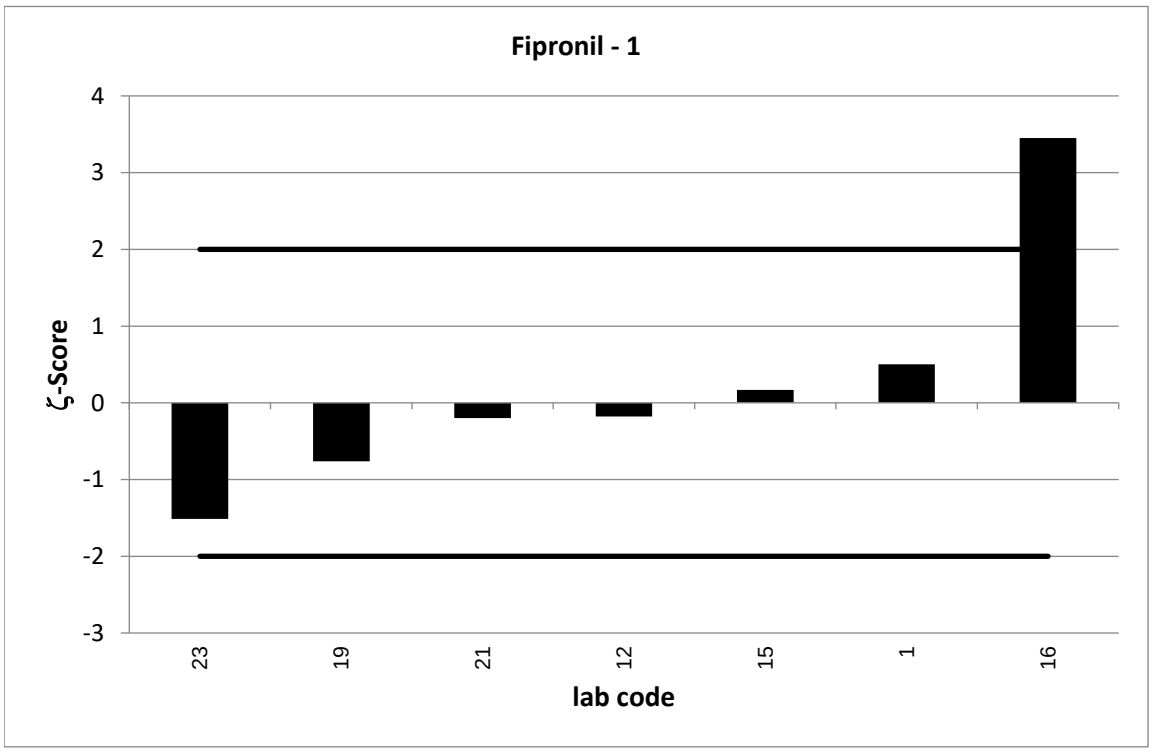
** s = satisfactory, q = questionable, u = unsatisfactory



Strongly deviating values are not shown in the diagram.

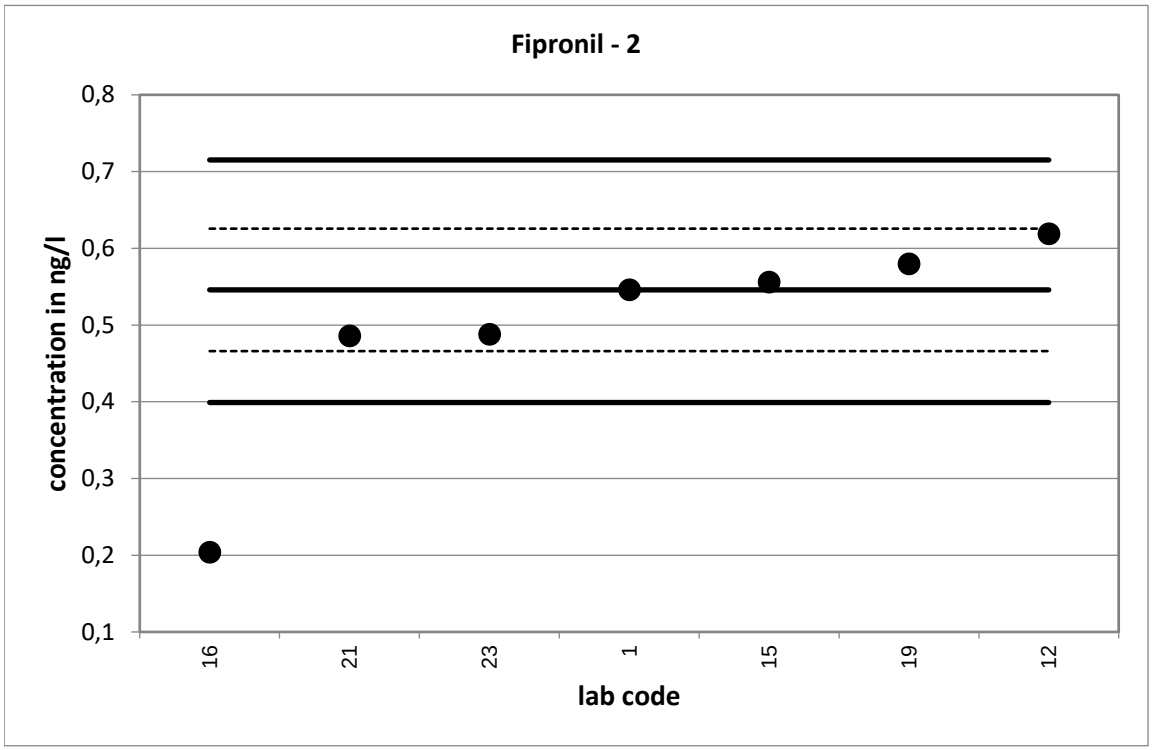



Fipronil - 1
expanded uncertainty in ng/l
0,14
0,12
0,1
0,08
0,06
0,04
0,02
0
16
23
19
12
15
1
21
lab code

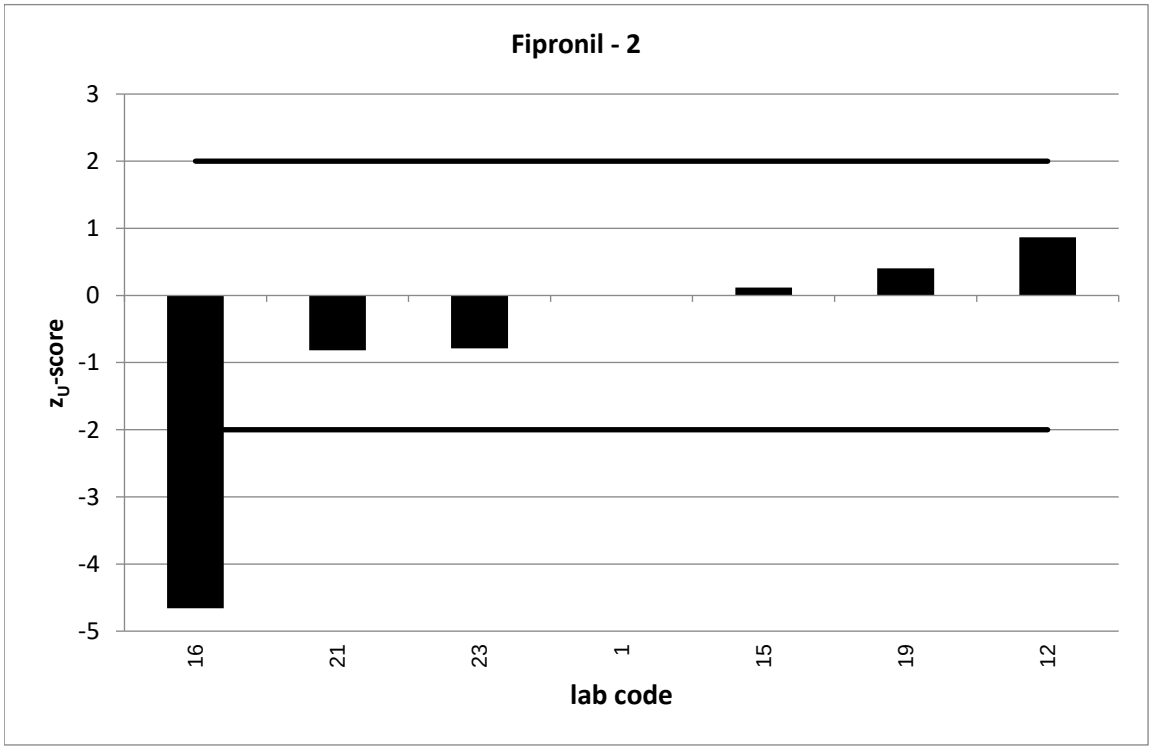

Fipronil - 1
ζ-Score
4
3
2
1
0
-1
-2
-3
23
19
21
12
15
1
16
lab code

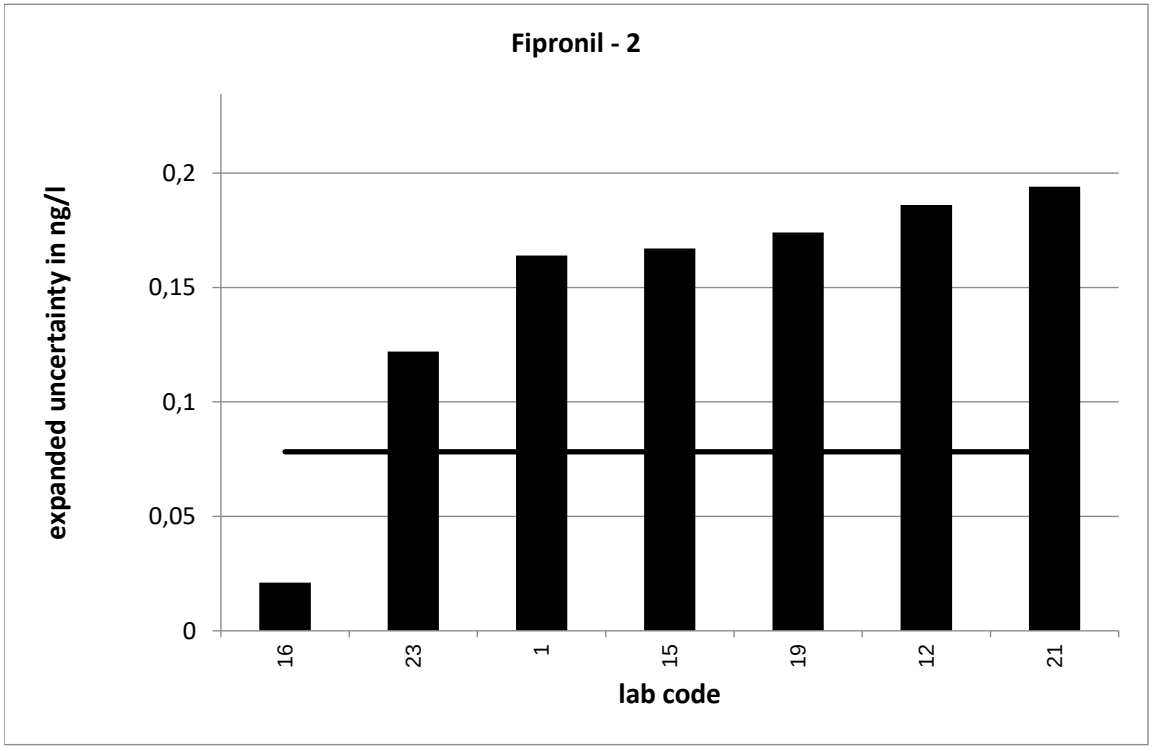
PT 4/24 - Pyrethroids		Fipronil - 2			
assigned value [ng/l]*			0,5458	± 0,0798	
upper tolerance limit [ng/l]			0,7152		
lower tolerance limit [ng/l]			0,399		
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,546	0,164	0,0	0,0	s
12	0,619	0,186	0,7	0,9	s
15	0,556	0,167	0,1	0,1	s
16	0,204	0,021	-8,3	-4,7	u
19	0,58	0,174	0,4	0,4	s
21	0,486	0,194	-0,6	-0,8	s
23	0,488	0,122	-0,8	-0,8	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%
** s = satisfactory, q = questionable, u = unsatisfactory

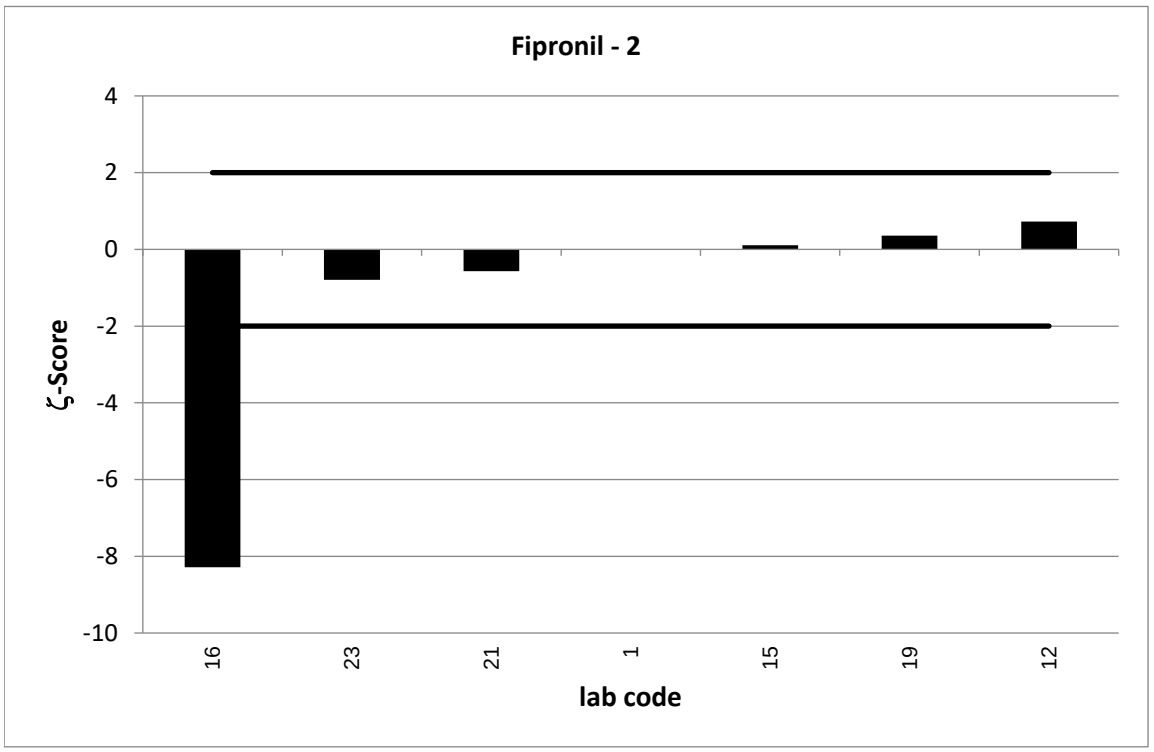


Strongly deviating values are not shown in the diagram.



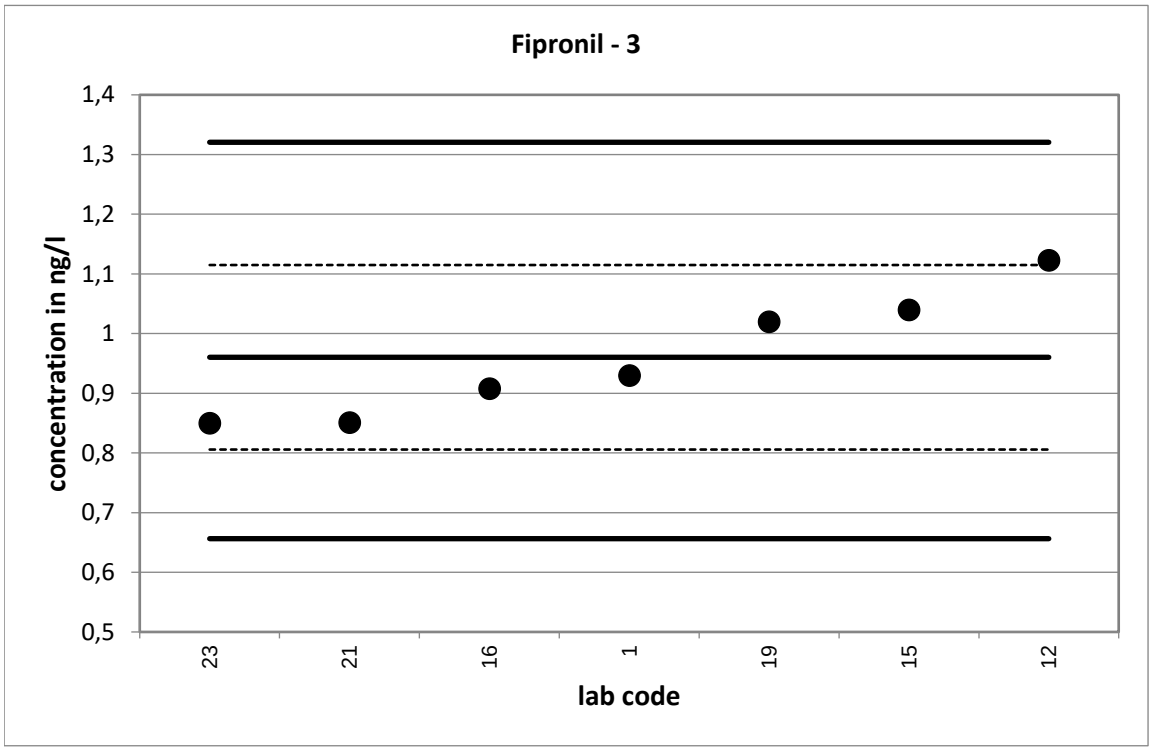


Strongly deviating values are not correctly shown in the diagram.

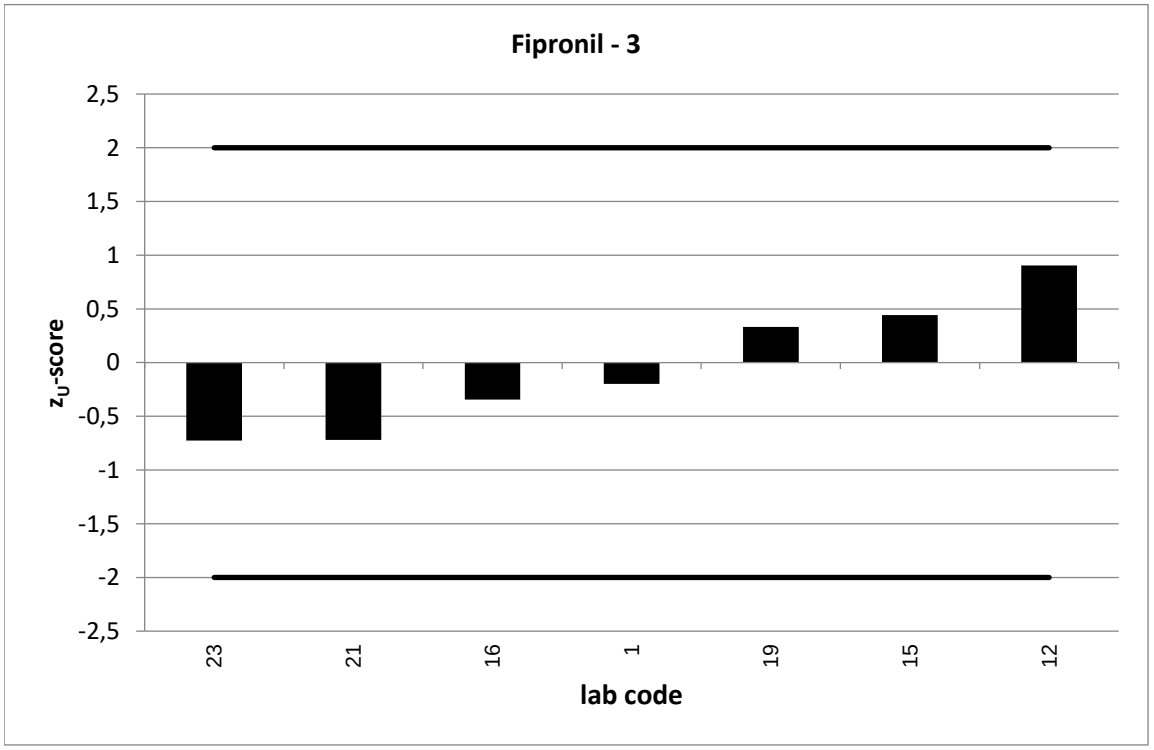


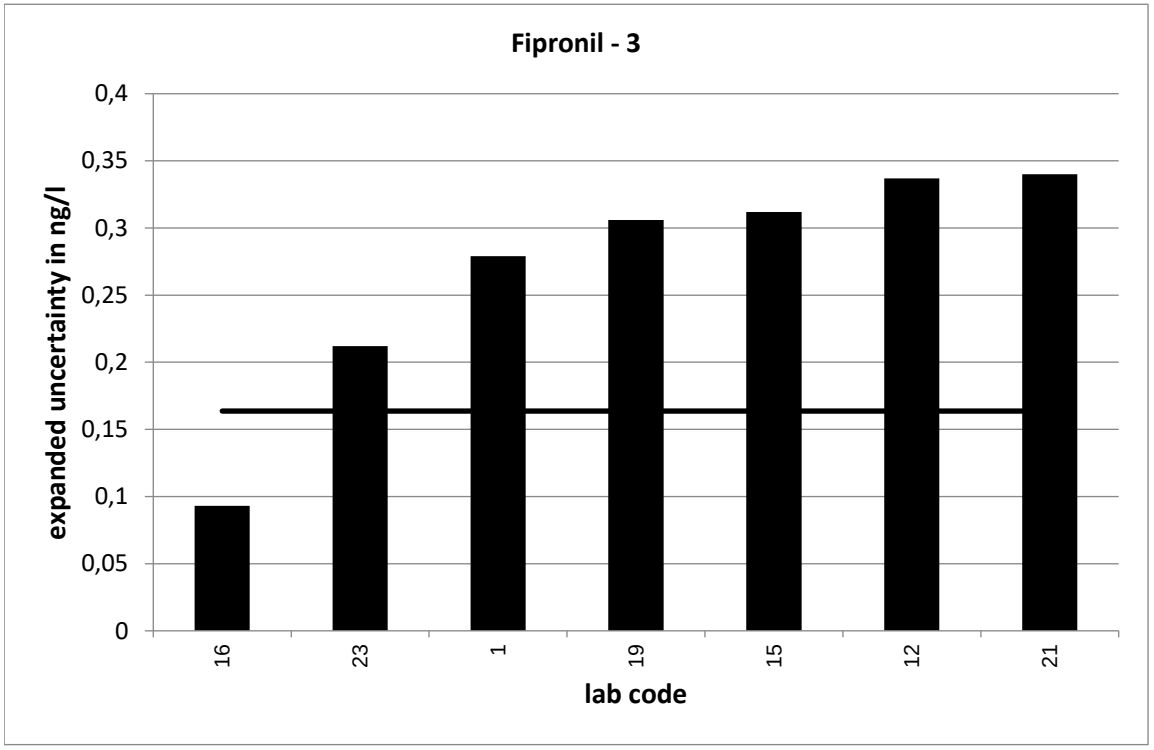
PT 4/24 - Pyrethroids		Fipronil - 3			
assigned value [ng/l]*			0,9603	± 0,1546	
upper tolerance limit [ng/l]			1,321		
lower tolerance limit [ng/l]			0,6563		
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,93	0,279	-0,2	-0,2	s
12	1,123	0,337	0,9	0,9	s
15	1,04	0,312	0,5	0,4	s
16	0,908	0,093	-0,6	-0,3	s
19	1,02	0,306	0,3	0,3	s
21	0,851	0,34	-0,6	-0,7	s
23	0,85	0,212	-0,8	-0,7	s

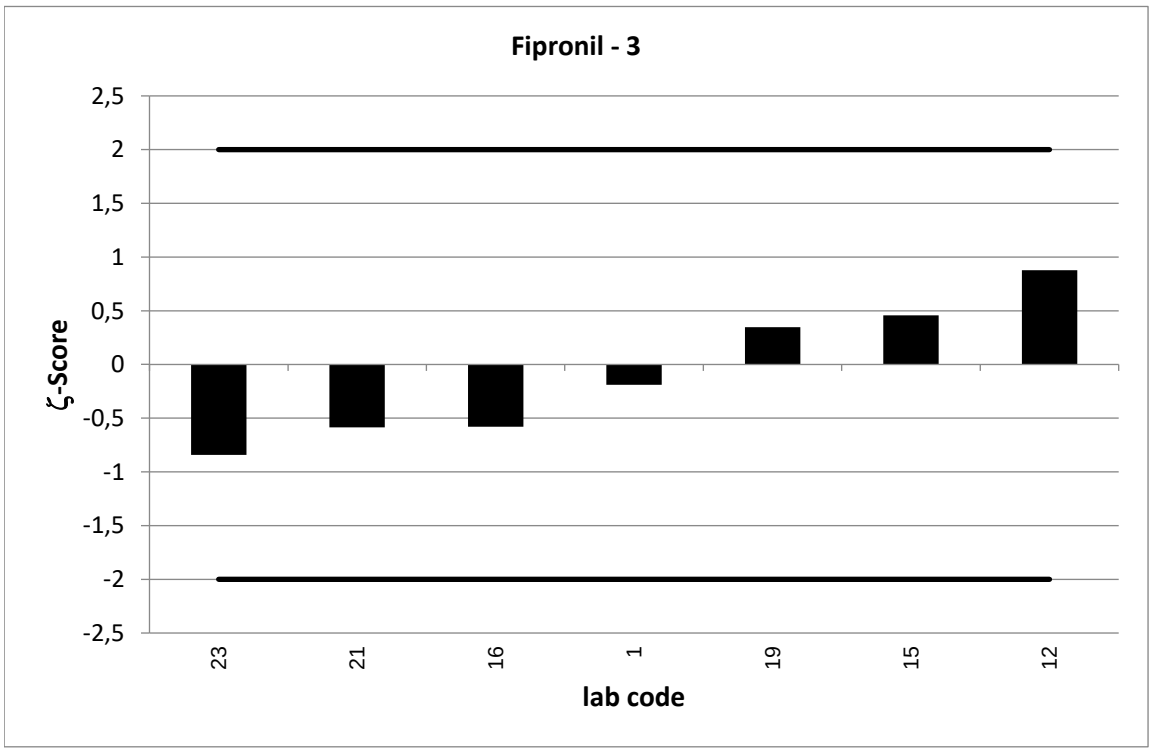
* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%
** s = satisfactory, q = questionable, u = unsatisfactory



Strongly deviating values are not shown in the diagram.



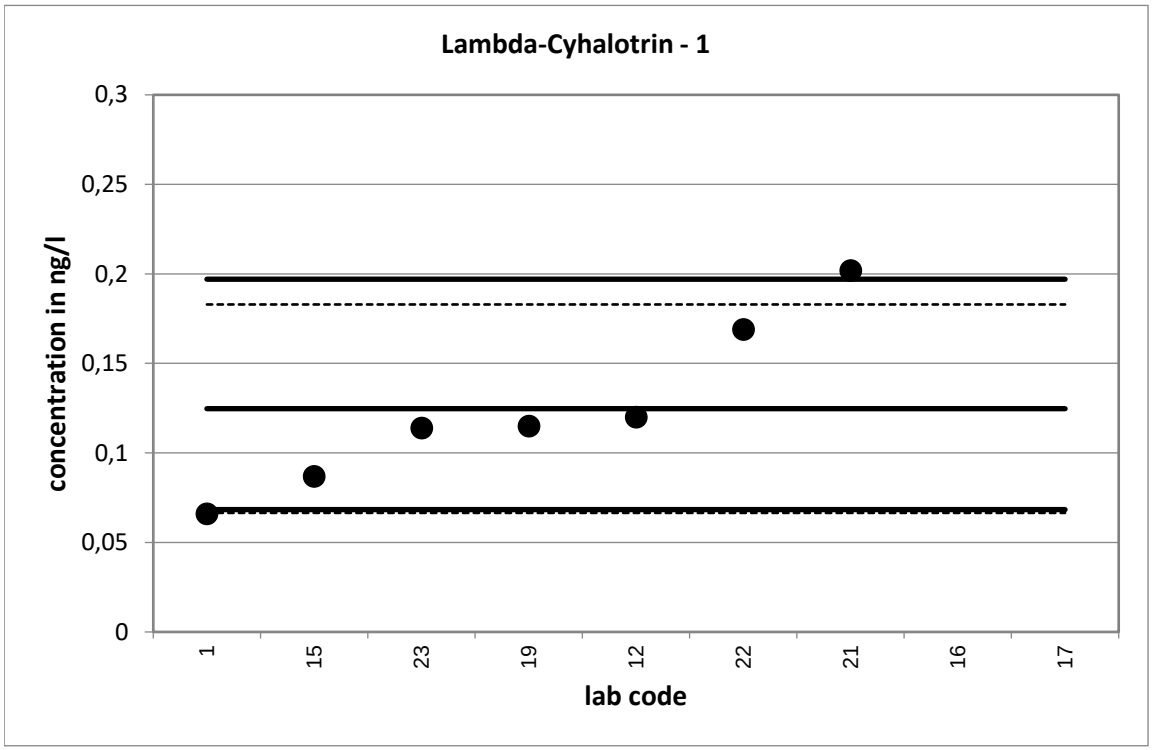

Fipronil - 3
expanded uncertainty in ng/l
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
16
23
1
19
15
12
21
lab code


Fipronil - 3
ζ-Score
2,5
2
1,5
1
0,5
0
-0,5
-1
-1,5
-2
-2,5
23
21
16
1
19
15
12
lab code

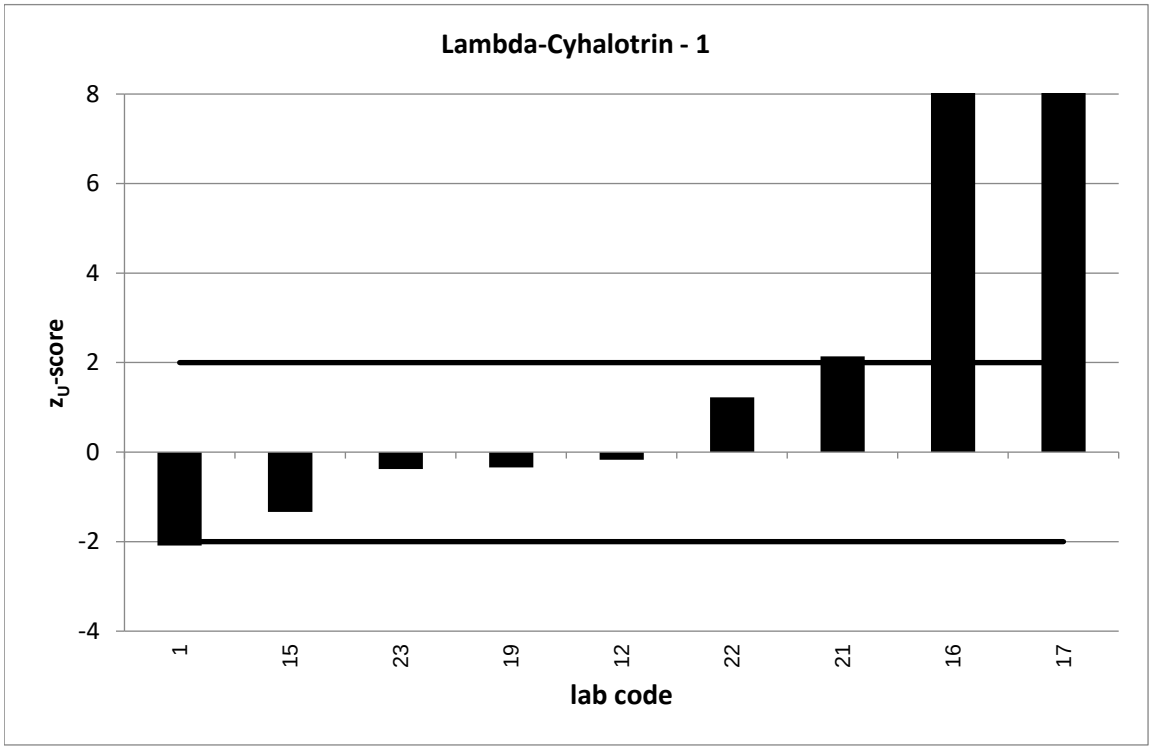
PT 4/24 - Pyrethroids		Lambda-Cyhalotrin - 1			
assigned value [ng/l]*		0,1247	± 0,0582		
upper tolerance limit [ng/l]		0,197			
lower tolerance limit [ng/l]		0,06836			
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,066	0,02	-1,9	-2,1	q
12	0,12	0,036	-0,1	-0,2	s
15	0,087	0,022	-1,2	-1,3	s
16	0,533	0,055	10,2	11,3	u
17	1,772	1,24	2,7	45,6	u
19	0,115	0,017	-0,3	-0,3	s
21	0,202	0,101	1,3	2,1	q
22	0,169	0,024	1,4	1,2	s
23	0,114	0,028	-0,3	-0,4	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

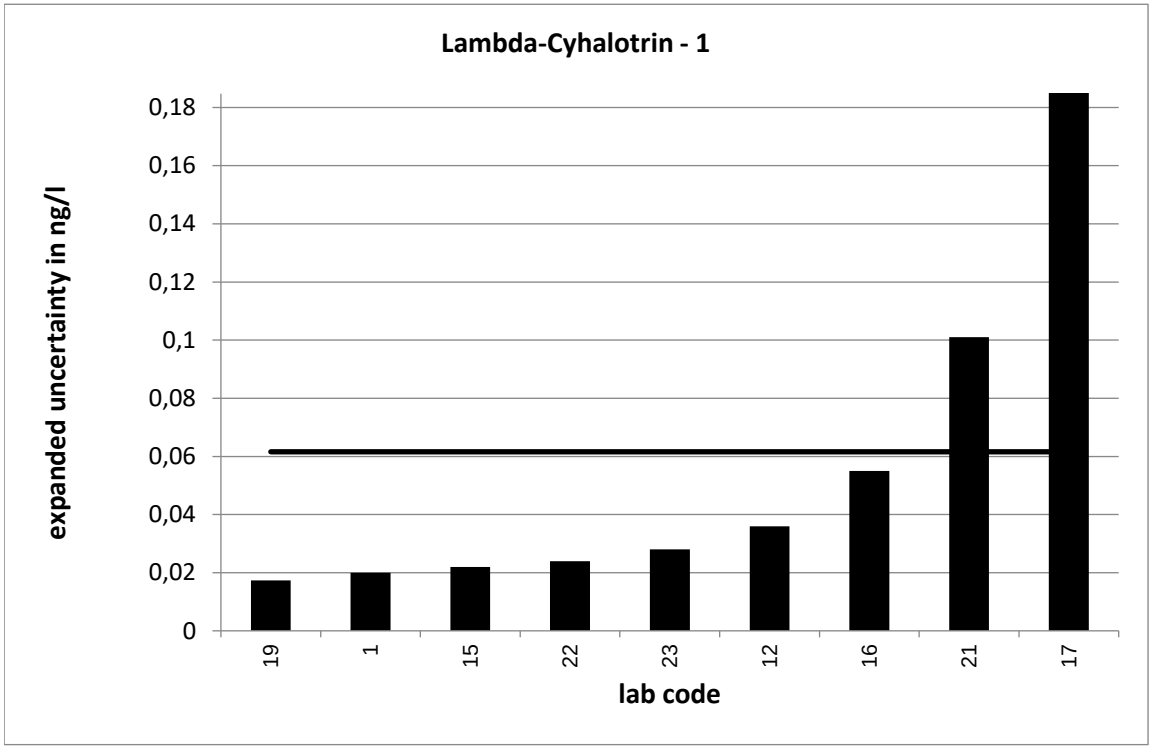
** s = satisfactory, q = questionable, u = unsatisfactory



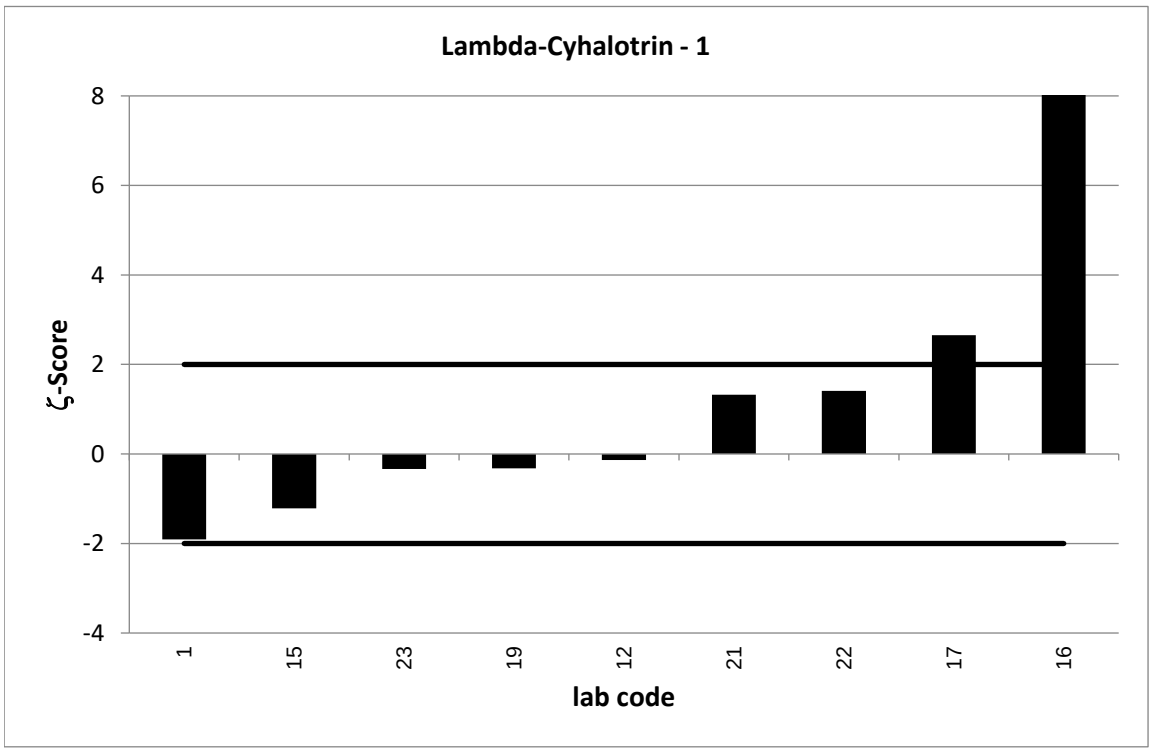
Strongly deviating values are not shown in the diagram.



Strongly deviating values are not correctly shown in the diagram.



Strongly deviating values are not correctly shown in the diagram.

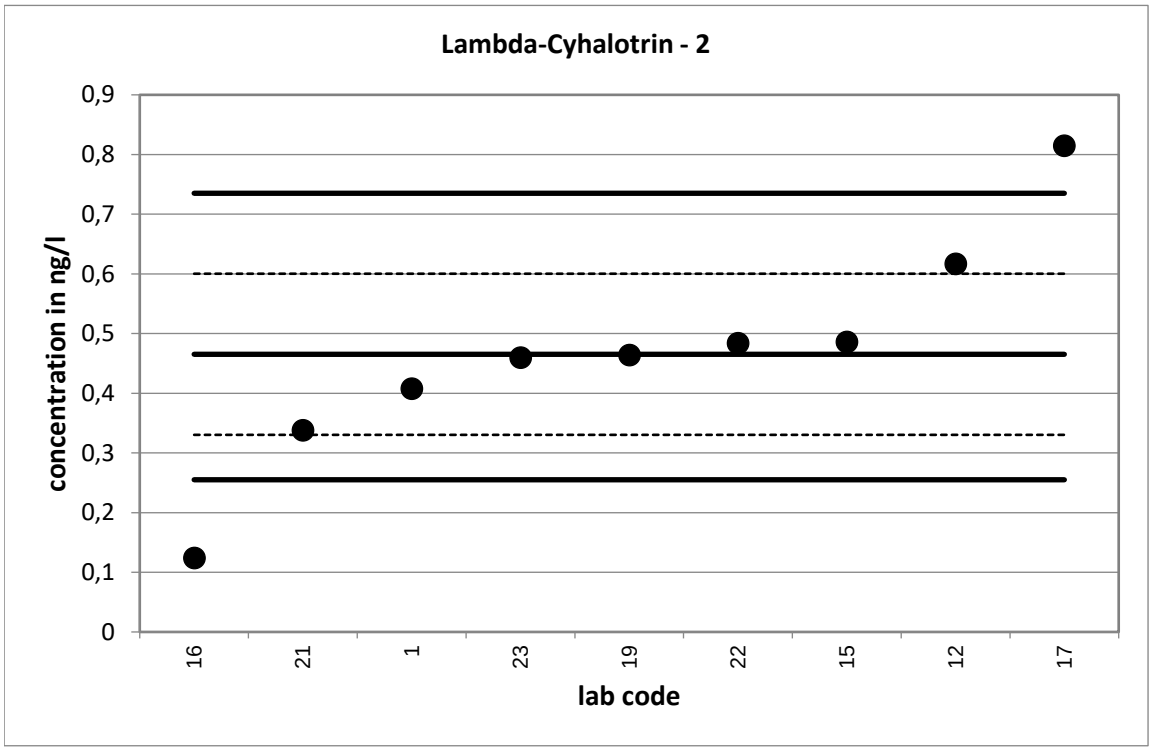


Strongly deviating values are not correctly shown in the diagram.

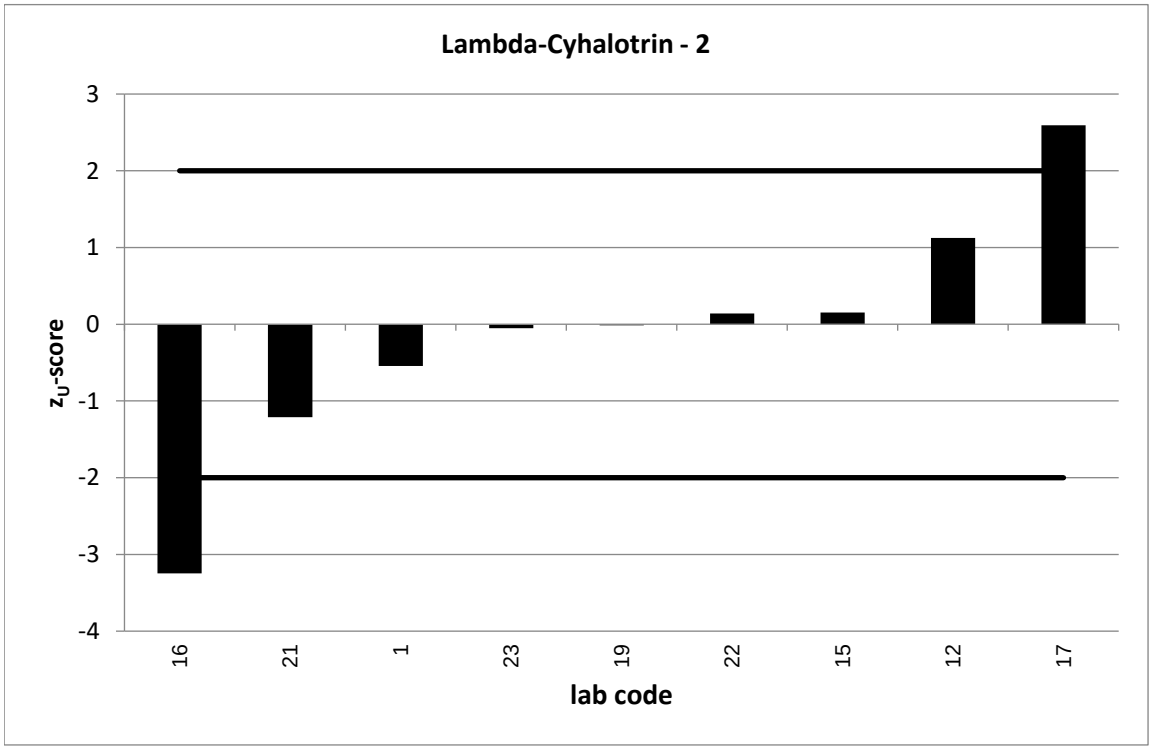
PT 4/24 - Pyrethroids		Lambda-Cyhalotrin - 2			
assigned value [ng/l]*		0,4653	± 0,135		
upper tolerance limit [ng/l]		0,7351			
lower tolerance limit [ng/l]		0,255			
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,408	0,122	-0,6	-0,5	s
12	0,617	0,185	1,3	1,1	s
15	0,486	0,122	0,2	0,2	s
16	0,124	0,013	-5,0	-3,2	u
17	0,815	0,57	1,2	2,6	q
19	0,464	0,07	0,0	0,0	s
21	0,338	0,169	-1,2	-1,2	s
22	0,484	0,069	0,2	0,1	s
23	0,46	0,115	-0,1	-0,1	s

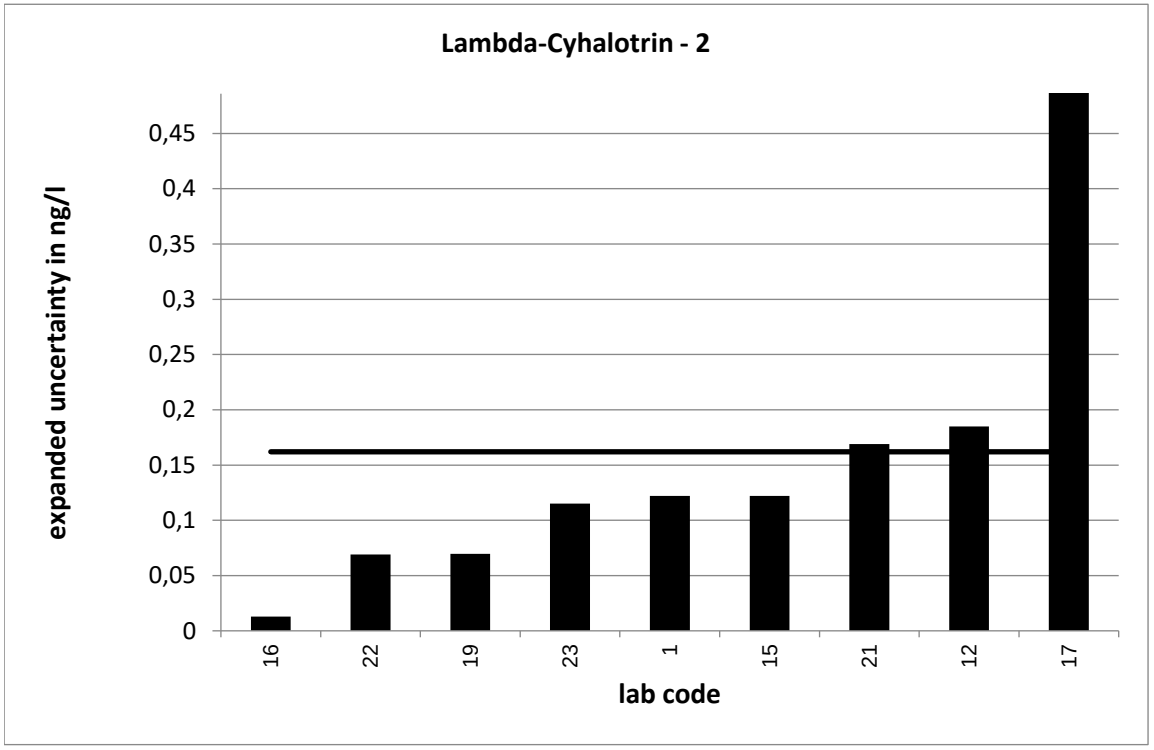
* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

** s = satisfactory, q = questionable, u = unsatisfactory

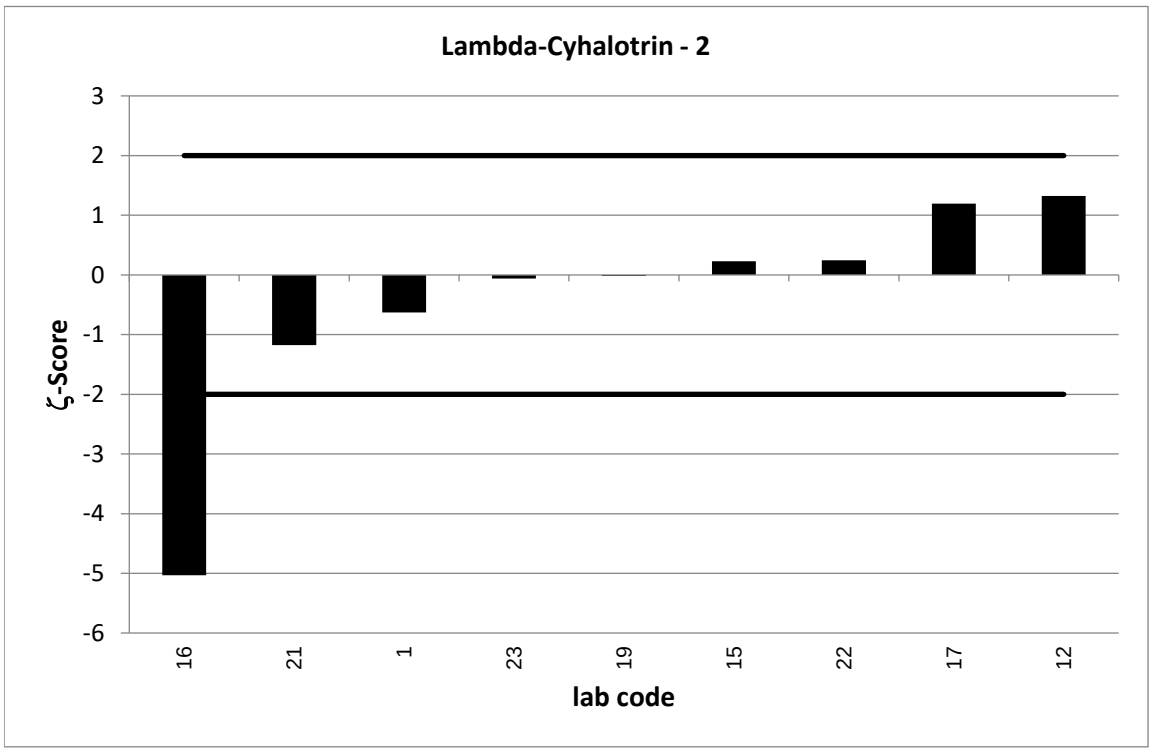


Strongly deviating values are not shown in the diagram.





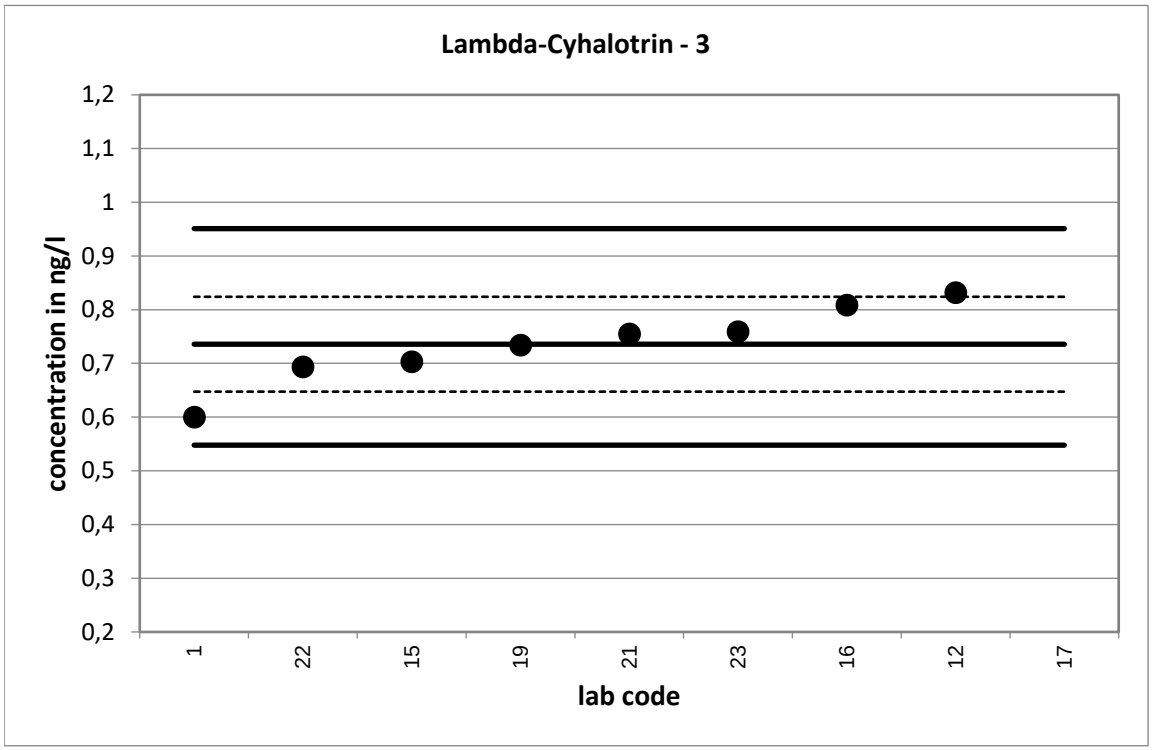
Strongly deviating values are not correctly shown in the diagram.



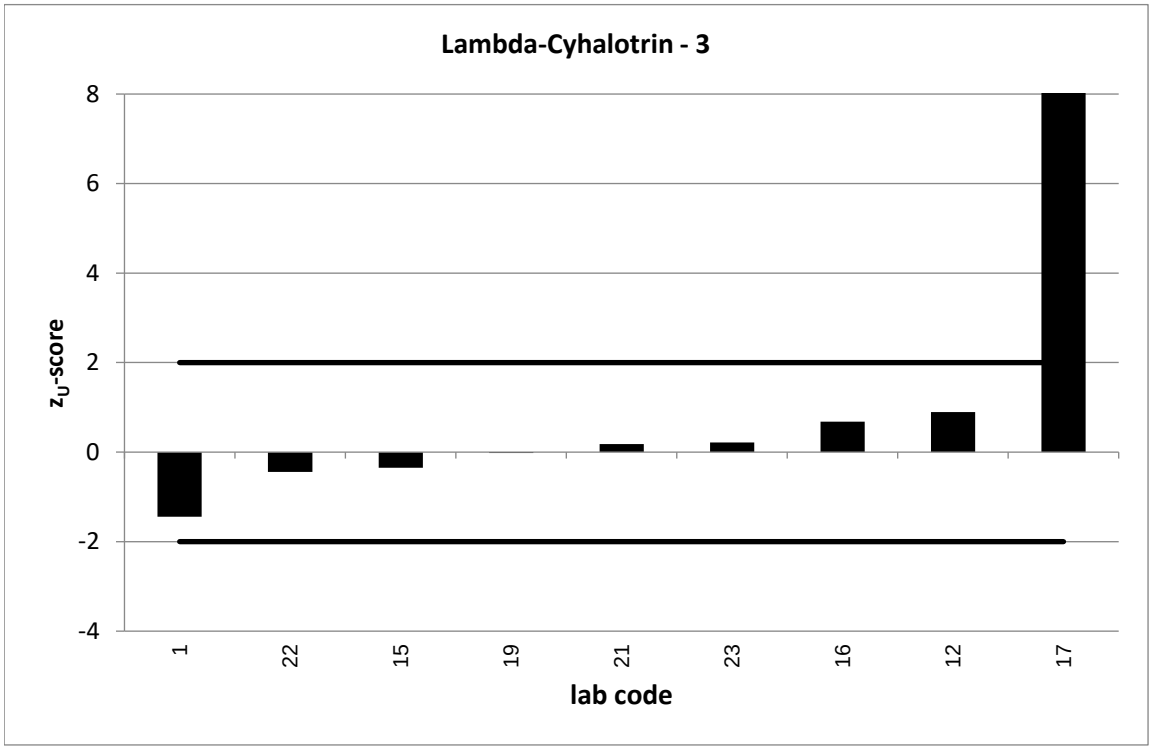
PT 4/24 - Pyrethroids		Lambda-Cyhalotrin - 3			
assigned value [ng/l]*			0,7358	± 0,0883	
upper tolerance limit [ng/l]			0,9509		
lower tolerance limit [ng/l]			0,5478		
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,6	0,18	-1,4	-1,4	s
12	0,832	0,25	0,7	0,9	s
15	0,703	0,176	-0,3	-0,3	s
16	0,809	0,084	1,2	0,7	s
17	2,442	1,709	2,0	15,9	u
19	0,734	0,11	0,0	0,0	s
21	0,755	0,377	0,1	0,2	s
22	0,694	0,099	-0,6	-0,4	s
23	0,759	0,19	0,2	0,2	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

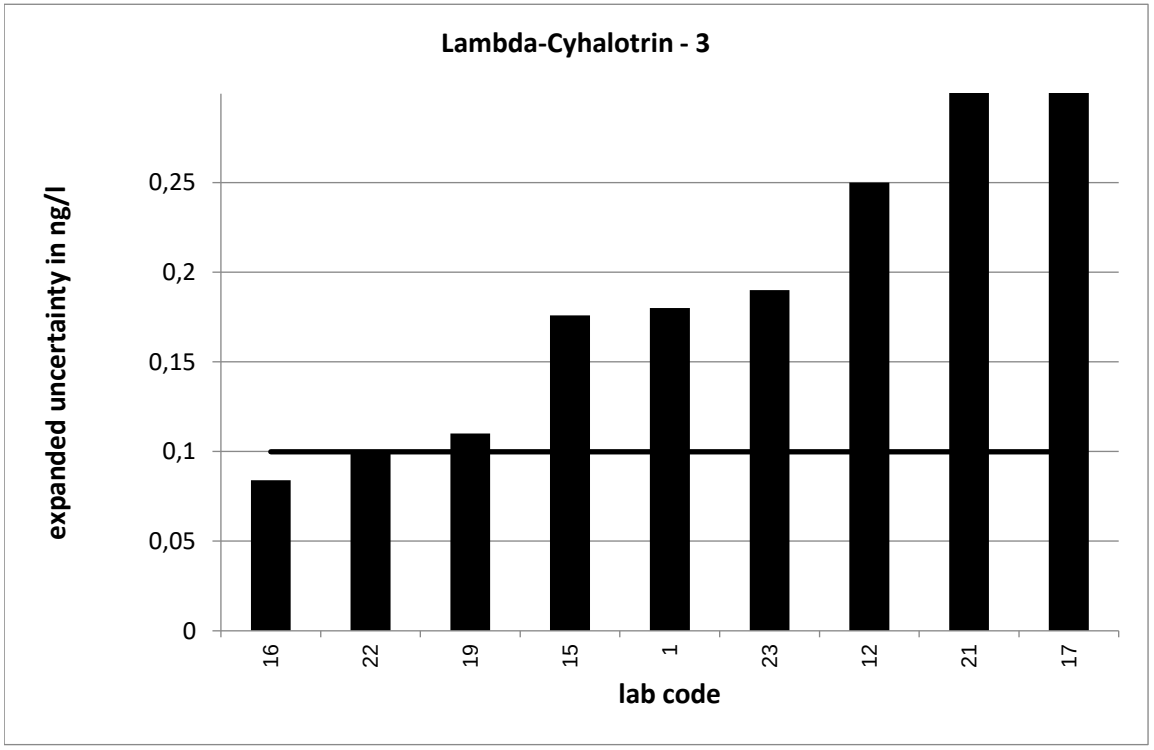
** s = satisfactory, q = questionable, u = unsatisfactory



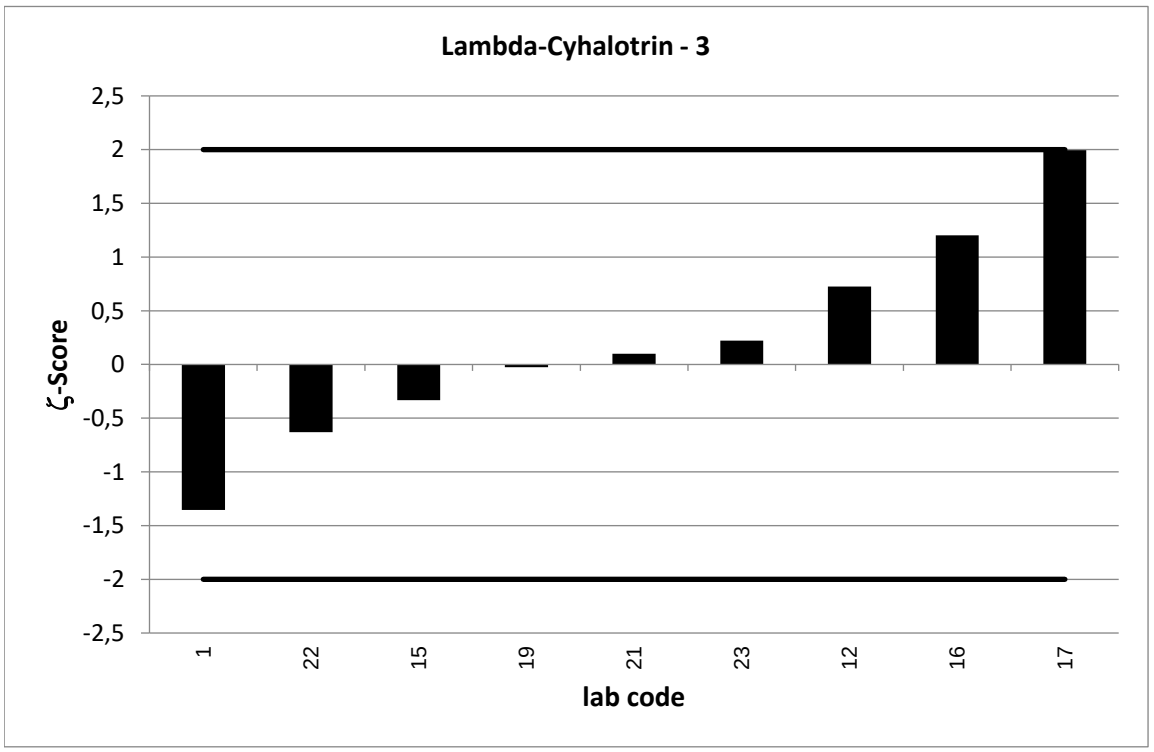
Strongly deviating values are not shown in the diagram.



Strongly deviating values are not correctly shown in the diagram.



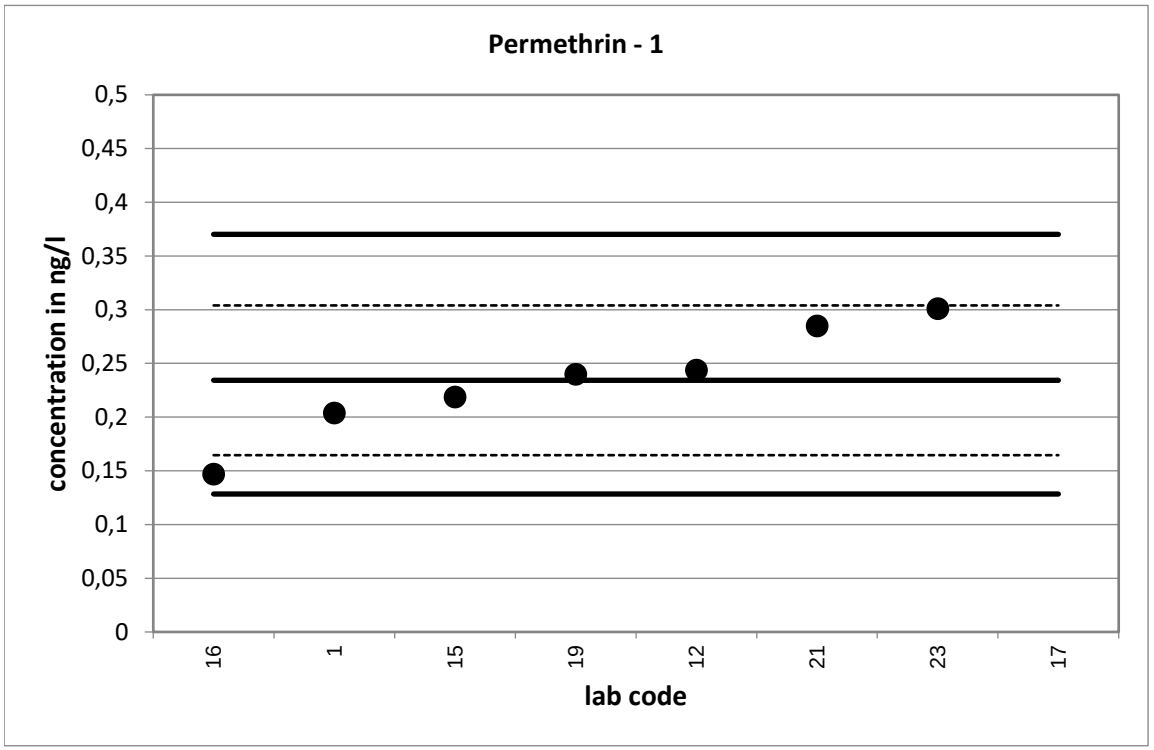
Strongly deviating values are not correctly shown in the diagram.



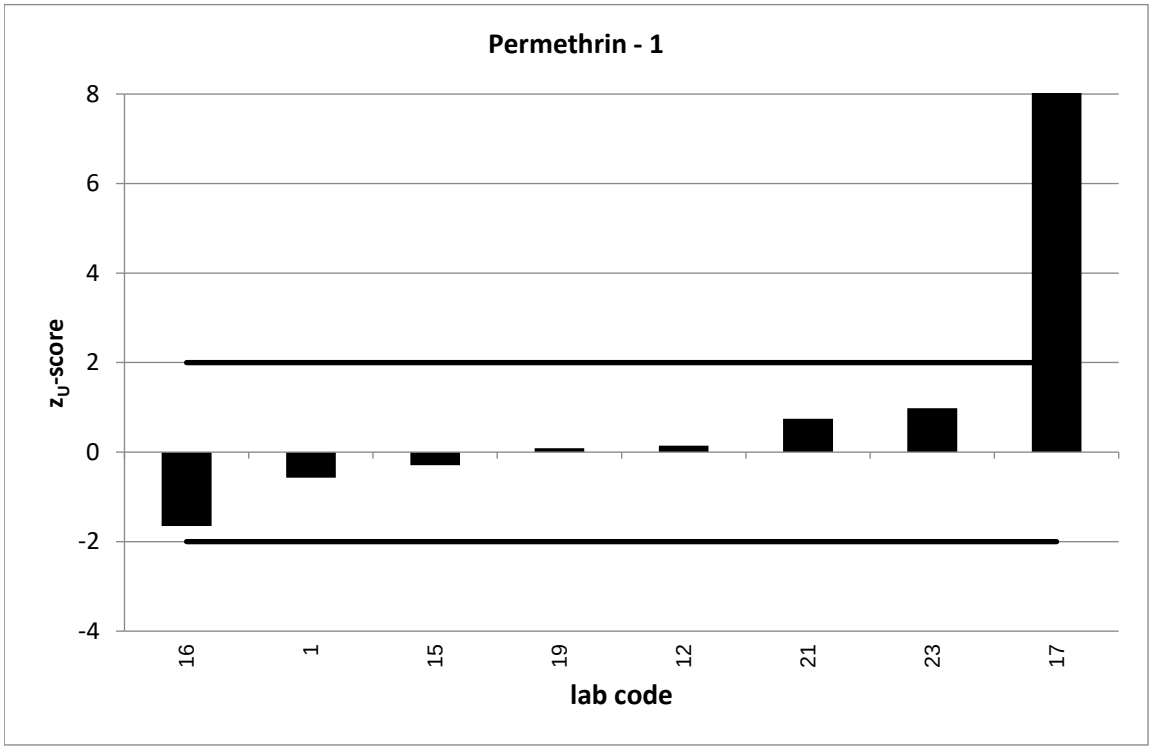
PT 4/24 - Pyrethroids		Permethrin - 1			
assigned value [ng/l]*		0,2343	± 0,0697		
upper tolerance limit [ng/l]		0,3701			
lower tolerance limit [ng/l]		0,1284			
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,204	0,061	-0,7	-0,6	s
12	0,244	0,073	0,2	0,1	s
15	0,219	0,044	-0,4	-0,3	s
16	0,147	0,035	-2,2	-1,6	s
17	1,429	1	2,4	17,6	u
19	0,24	0,072	0,1	0,1	s
21	0,285	0,143	0,6	0,7	s
23	0,301	0,135	0,9	1,0	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

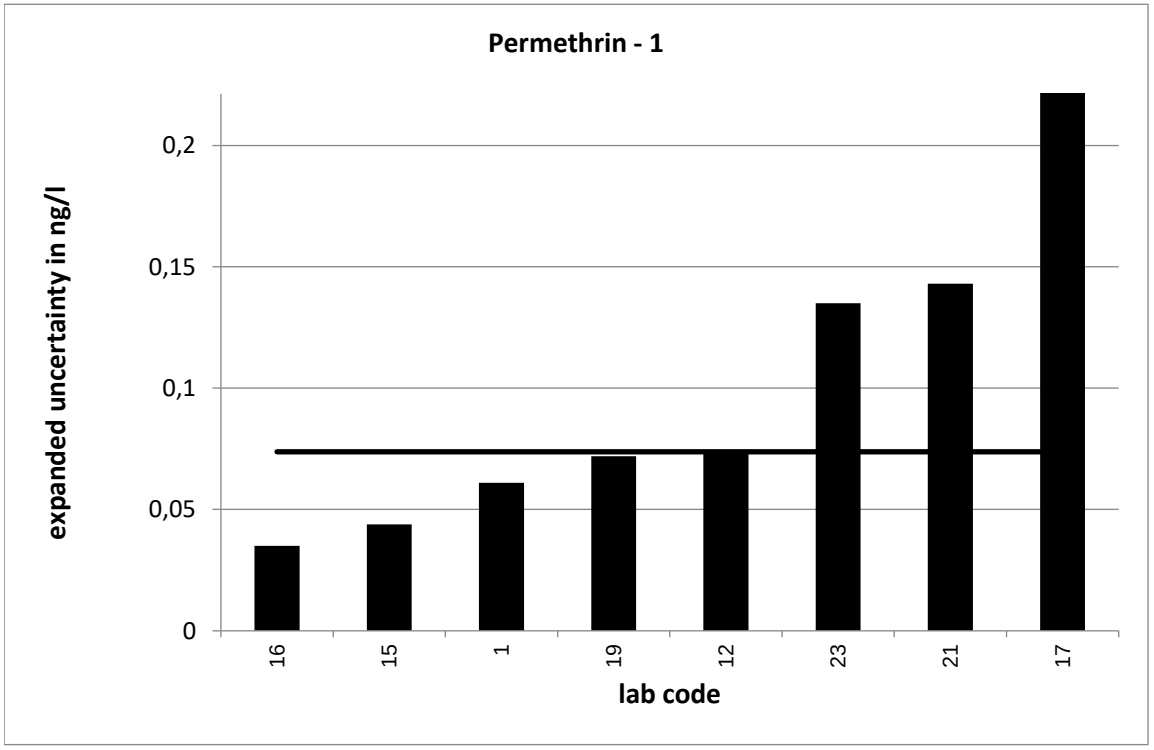
** s = satisfactory, q = questionable, u = unsatisfactory



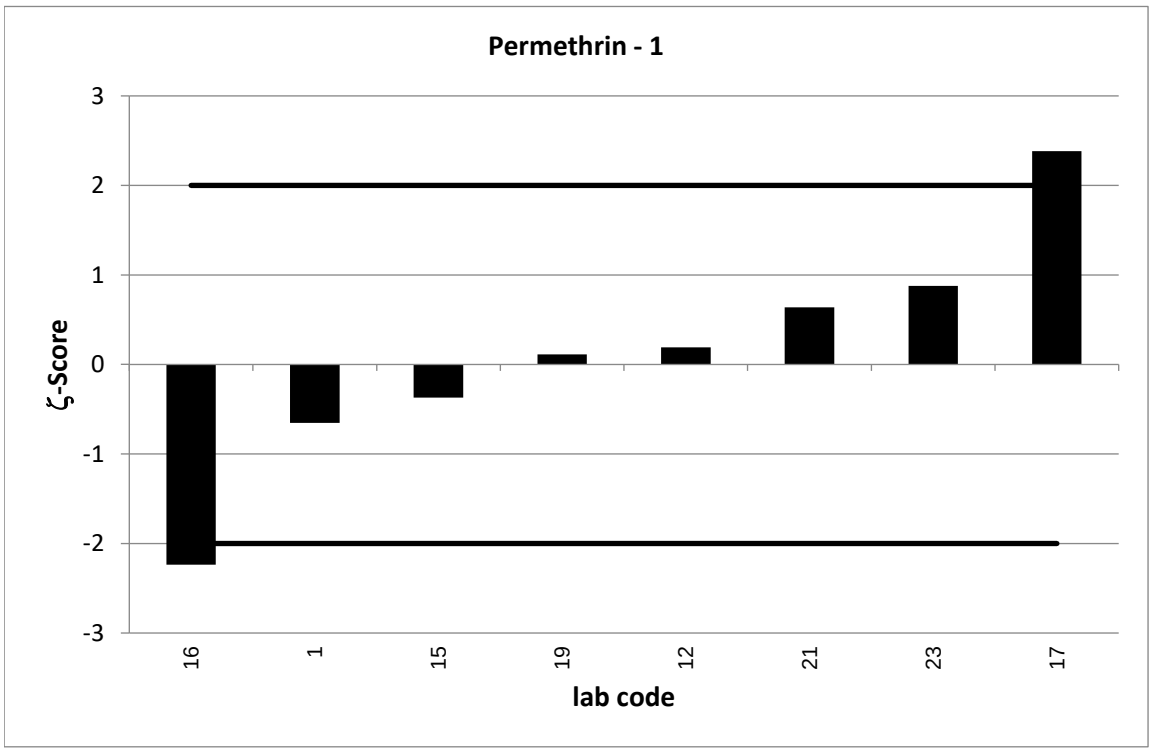
Strongly deviating values are not shown in the diagram.



Strongly deviating values are not correctly shown in the diagram.

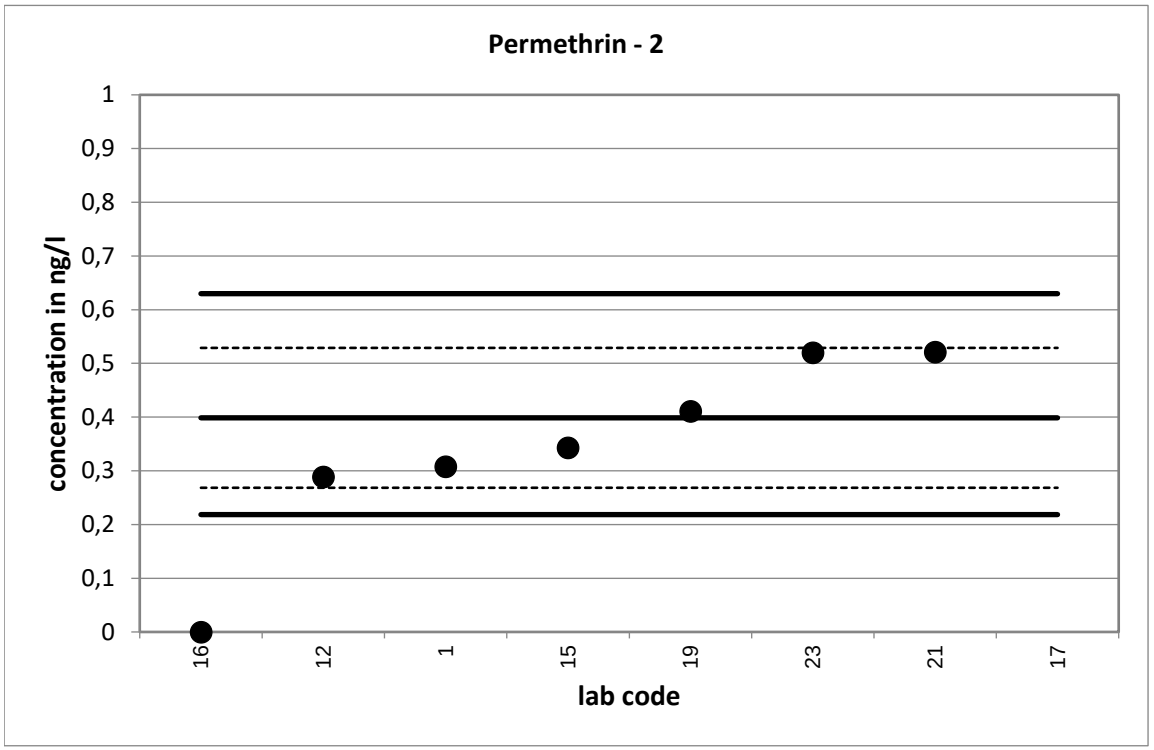


Strongly deviating values are not correctly shown in the diagram.

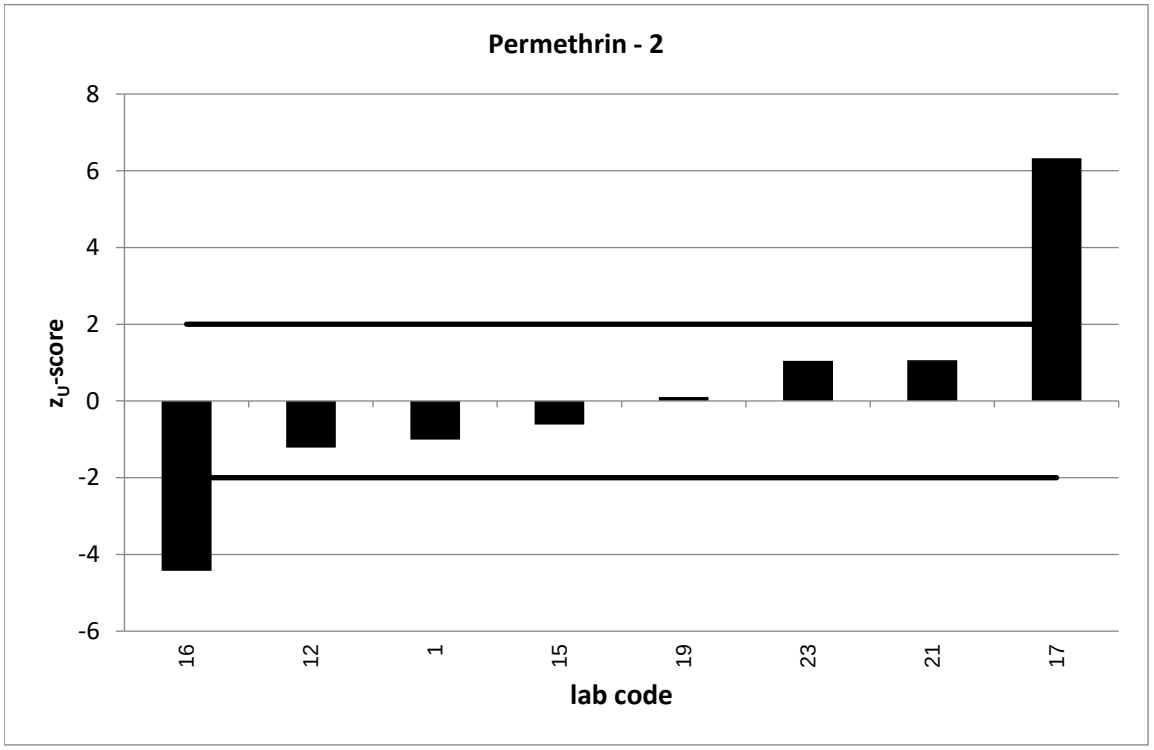


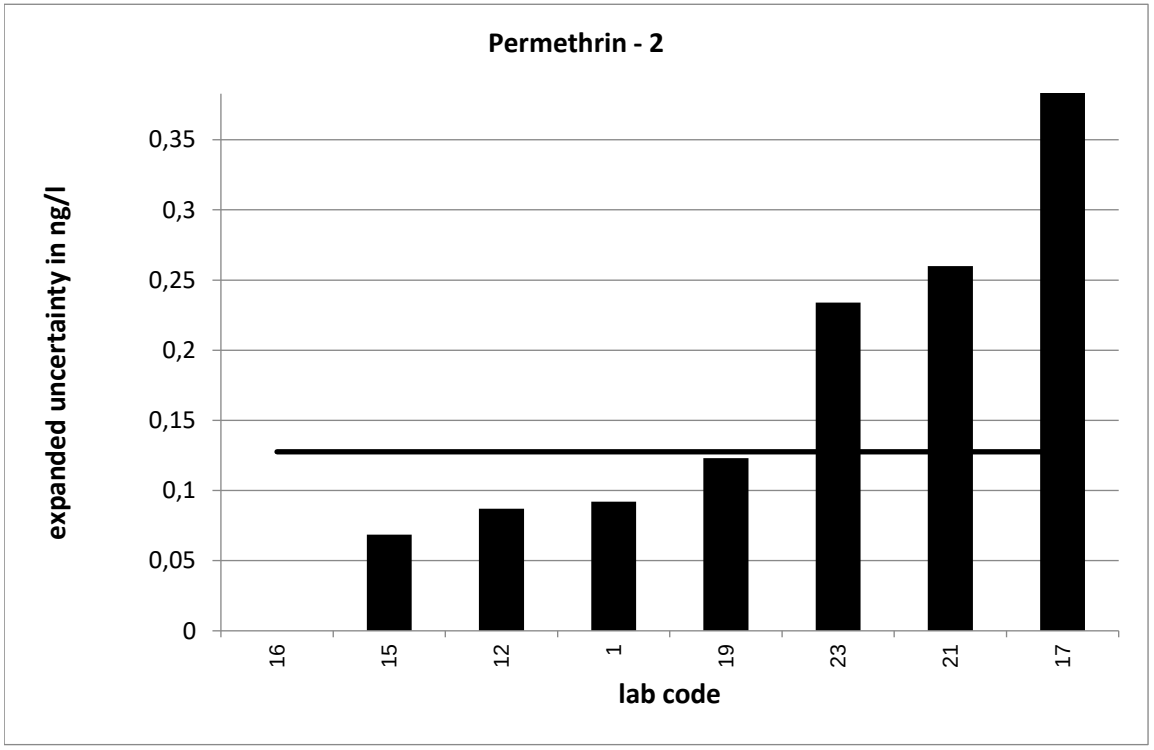
PT 4/24 - Pyrethroids		Permethrin - 2			
assigned value [ng/l]*			0,3987	± 0,1302	
upper tolerance limit [ng/l]			0,6298		
lower tolerance limit [ng/l]			0,2185		
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,308	0,092	-1,1	-1,0	s
12	0,289	0,087	-1,4	-1,2	s
15	0,343	0,069	-0,8	-0,6	s
16	0	0	-6,1	-4,4	u
17	1,13	0,791	1,8	6,3	u
19	0,411	0,123	0,1	0,1	s
21	0,521	0,26	0,8	1,1	s
23	0,52	0,234	0,9	1,0	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%
** s = satisfactory, q = questionable, u = unsatisfactory

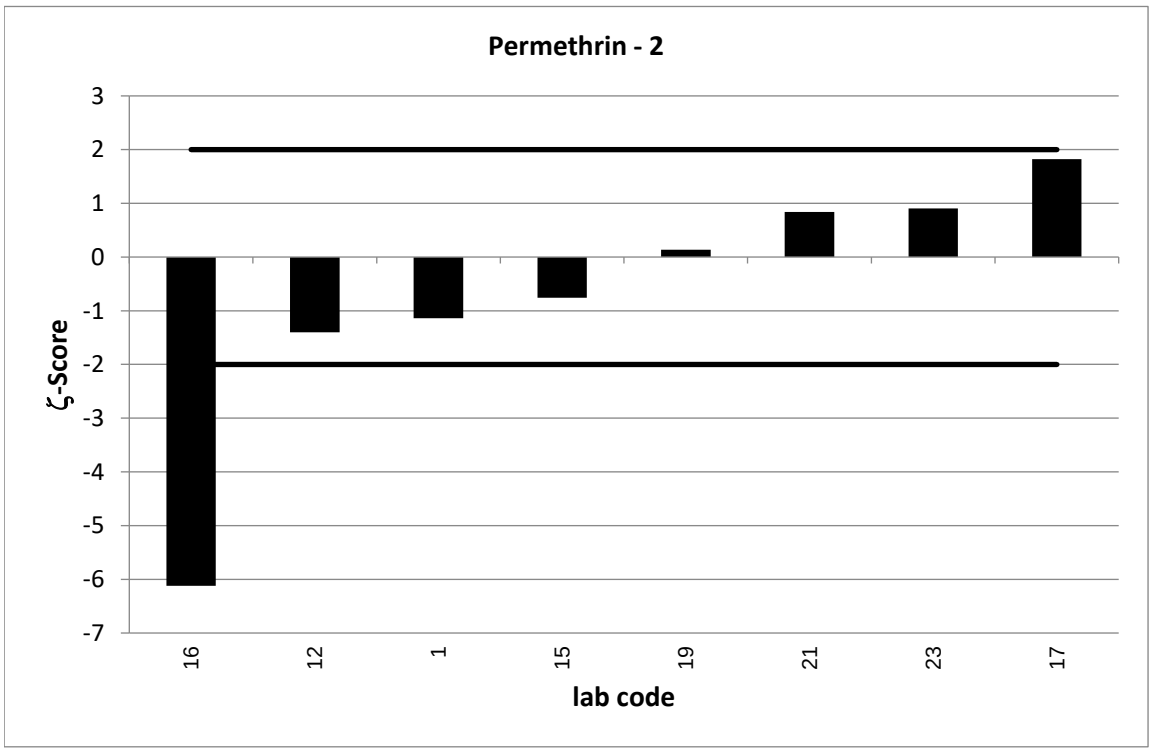


Strongly deviating values are not shown in the diagram.





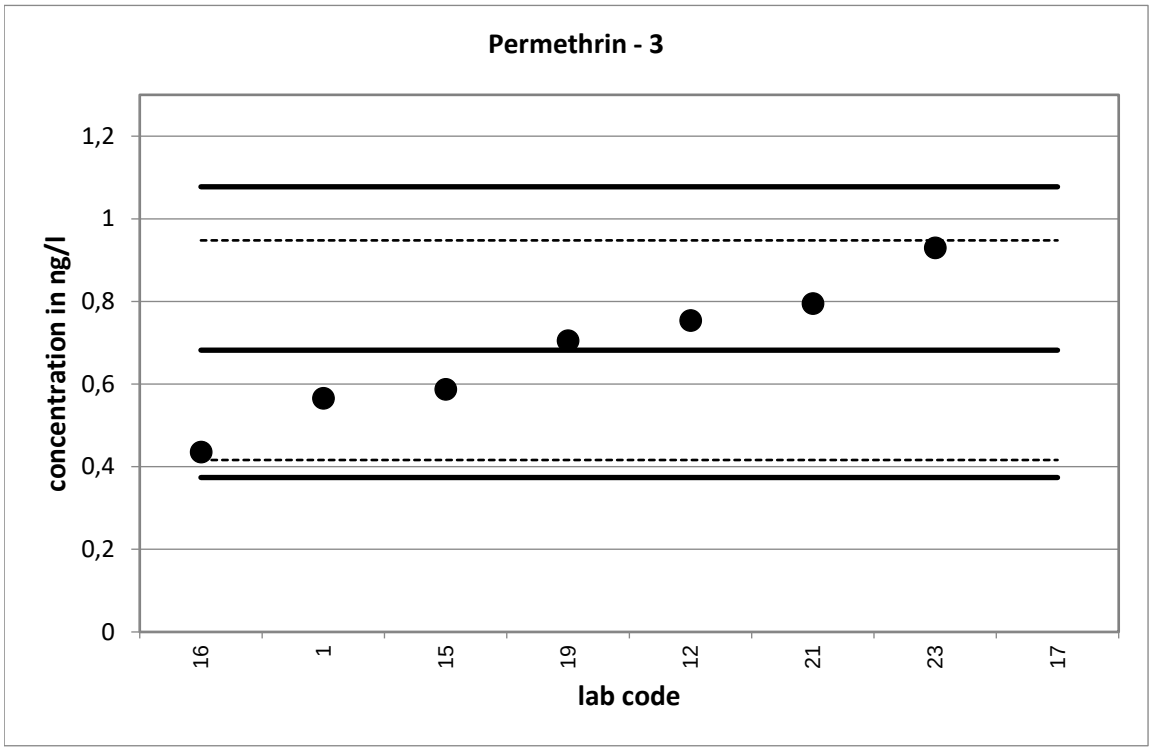
Strongly deviating values are not correctly shown in the diagram.



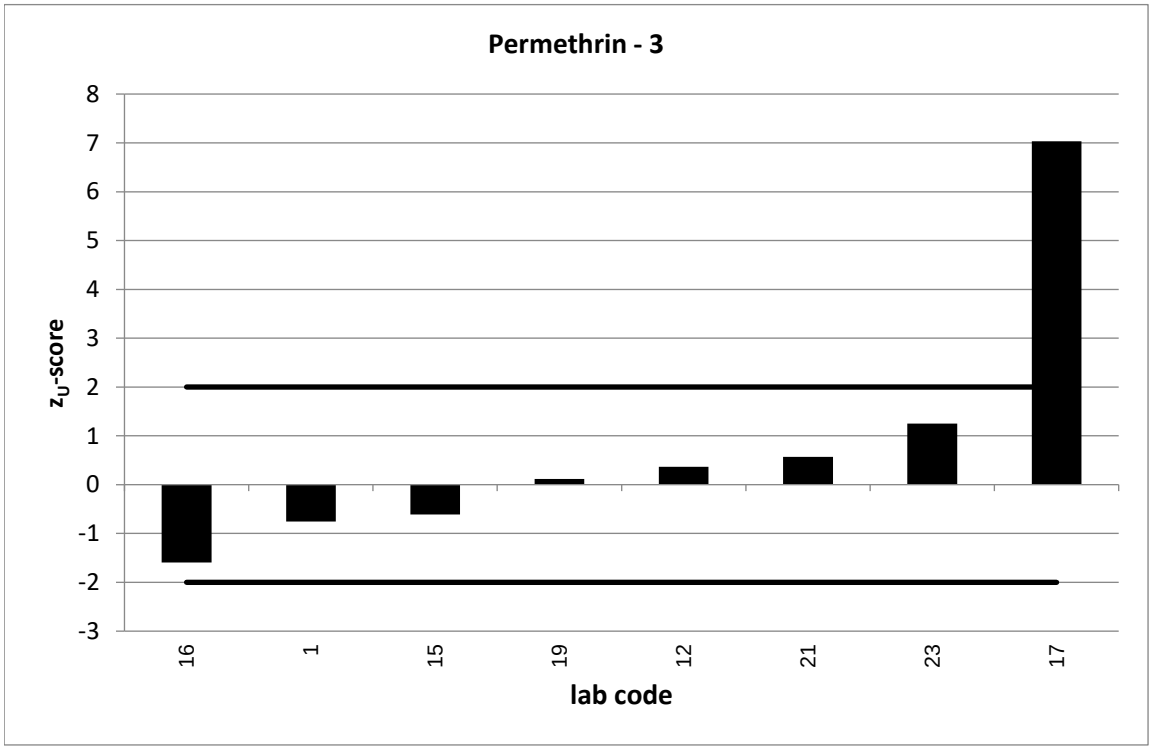
PT 4/24 - Pyrethroids		Permethrin - 3			
assigned value [ng/l]*			0,682	± 0,2658	
upper tolerance limit [ng/l]			1,077		
lower tolerance limit [ng/l]			0,3738		
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,566	0,17	-0,7	-0,8	s
12	0,754	0,226	0,4	0,4	s
15	0,588	0,118	-0,6	-0,6	s
16	0,436	0,103	-1,7	-1,6	s
17	2,072	1,45	1,9	7,0	u
19	0,705	0,212	0,1	0,1	s
21	0,795	0,397	0,5	0,6	s
23	0,93	0,418	1,0	1,3	s

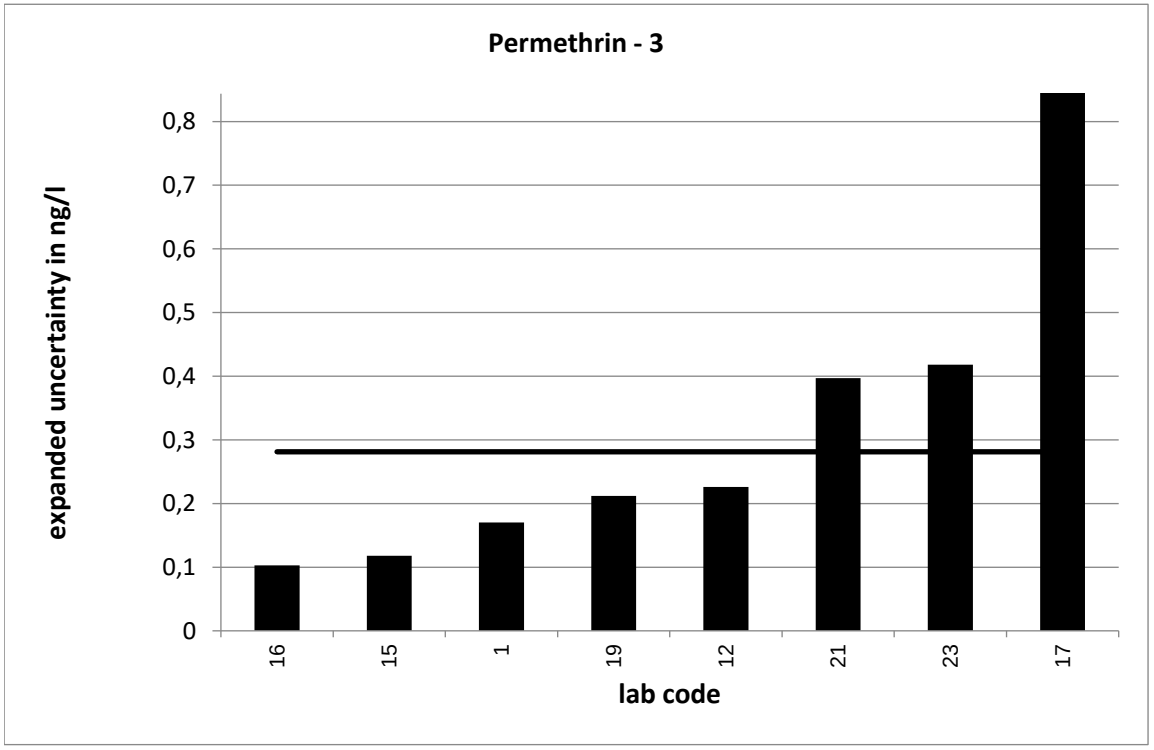
* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

** s = satisfactory, q = questionable, u = unsatisfactory

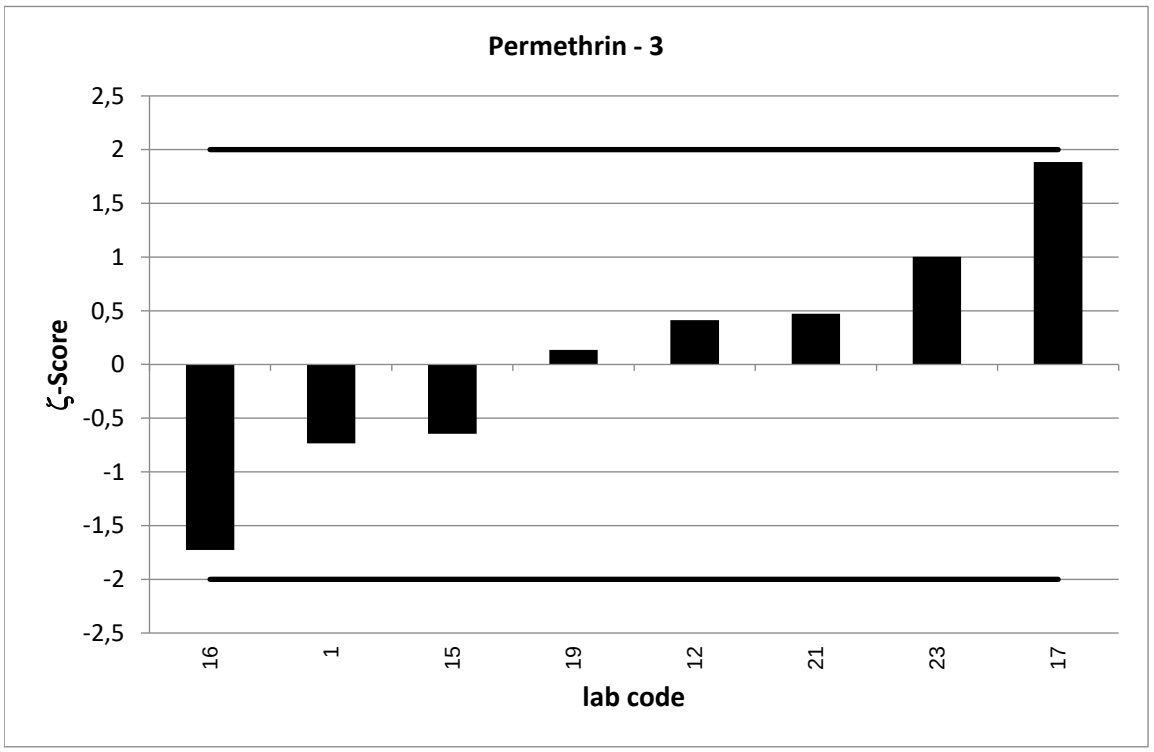


Strongly deviating values are not shown in the diagram.





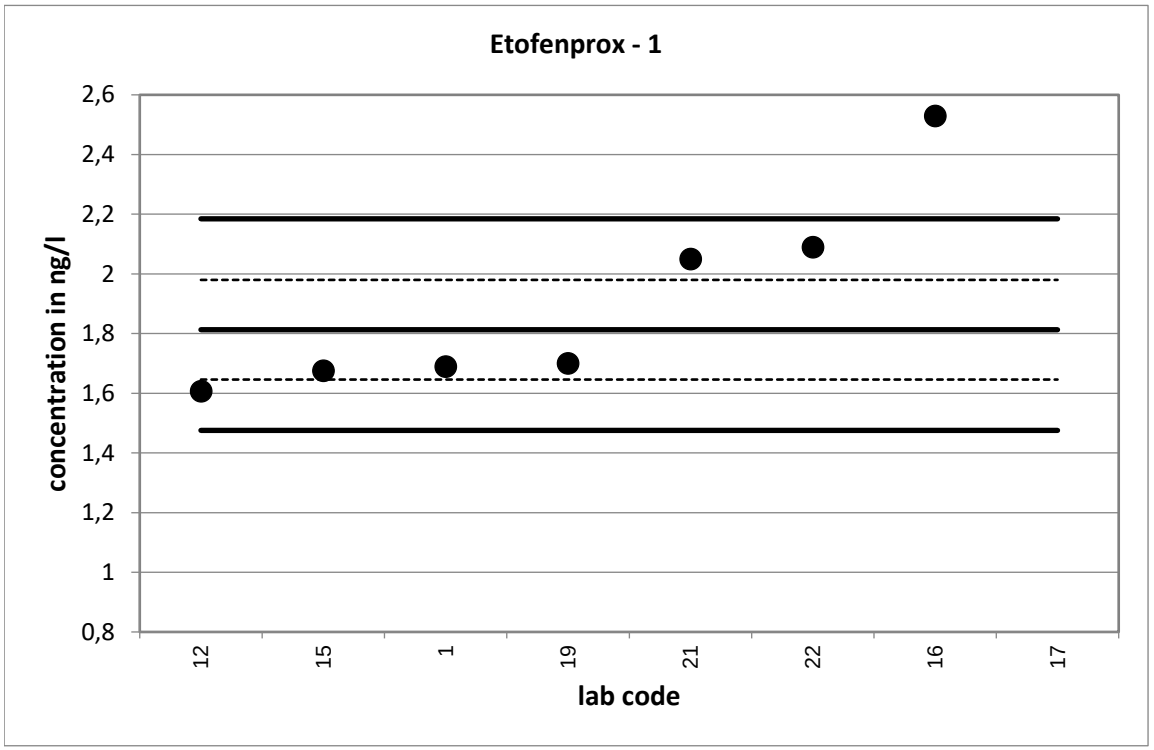
Strongly deviating values are not correctly shown in the diagram.



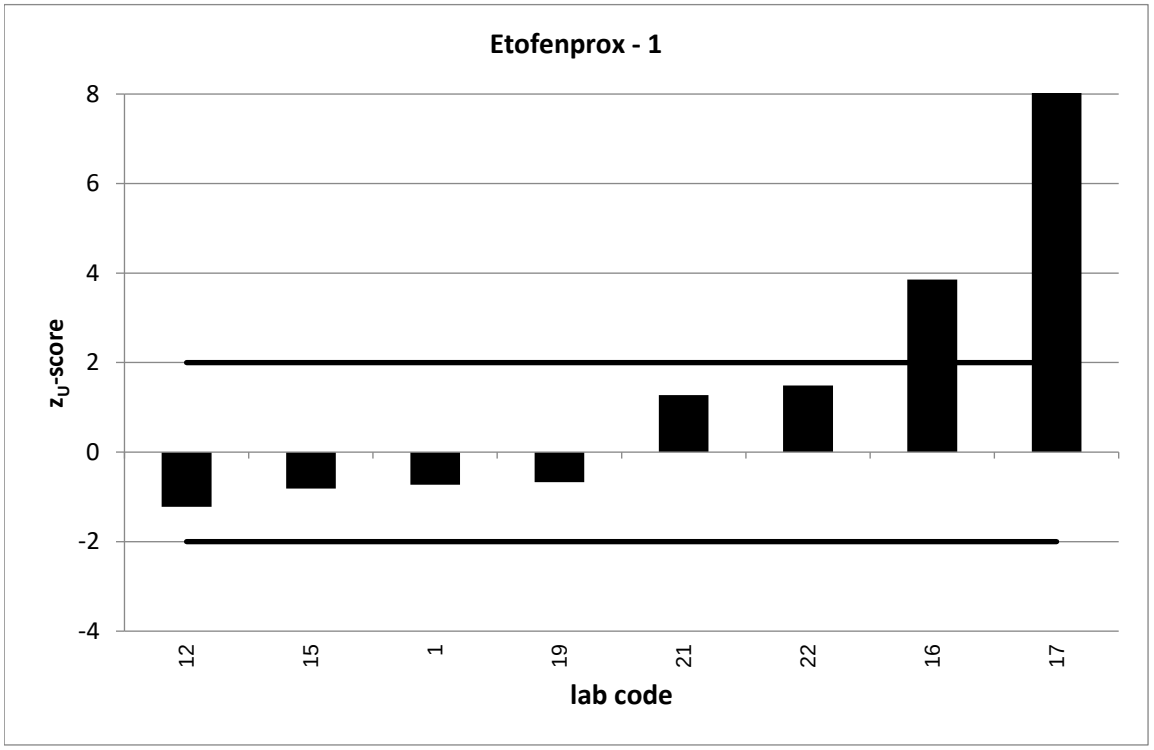
PT 4/24 - Pyrethroids		Etofenprox - 1			
assigned value [ng/l]*			1,813	± 0,167	
upper tolerance limit [ng/l]			2,185		
lower tolerance limit [ng/l]			1,476		
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	1,69	0,51	-0,5	-0,7	s
12	1,607	0,482	-0,8	-1,2	s
15	1,676	0,419	-0,6	-0,8	s
16	2,53	0,253	4,7	3,9	u
17	10,421	7,295	2,4	46,3	u
19	1,7	0,255	-0,7	-0,7	s
21	2,05	1,03	0,5	1,3	s
22	2,09	0,56	0,9	1,5	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

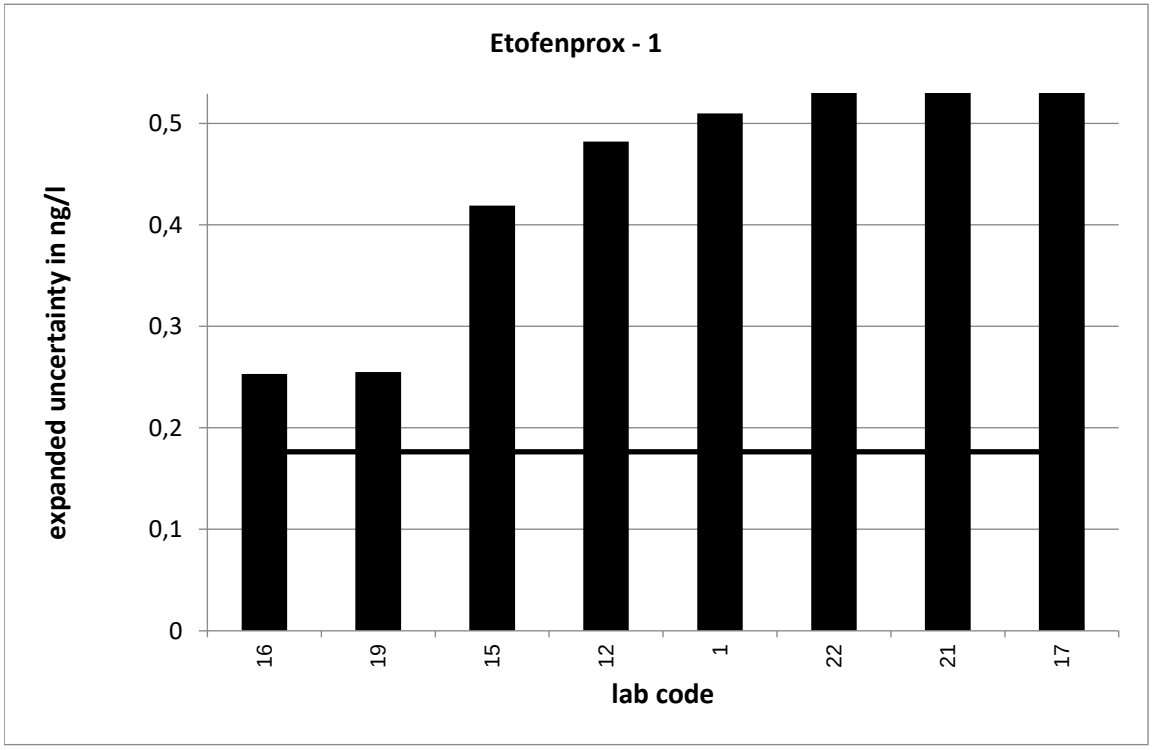
** s = satisfactory, q = questionable, u = unsatisfactory



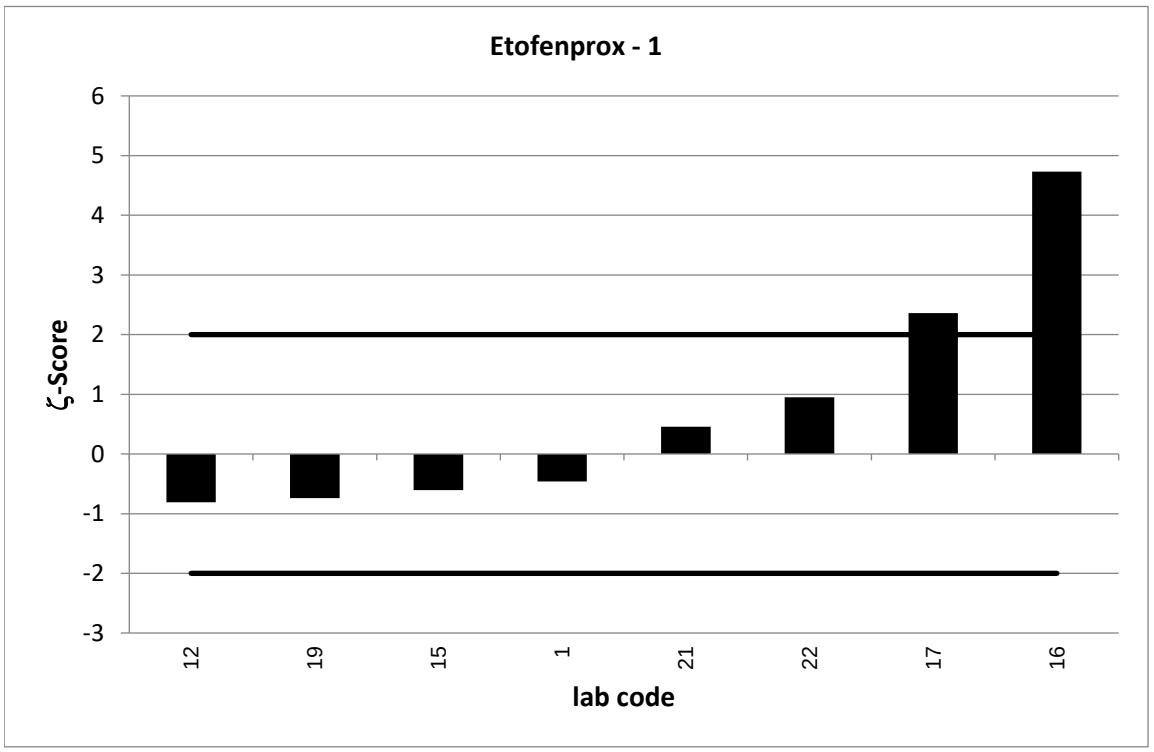
Strongly deviating values are not shown in the diagram.



Strongly deviating values are not correctly shown in the diagram.



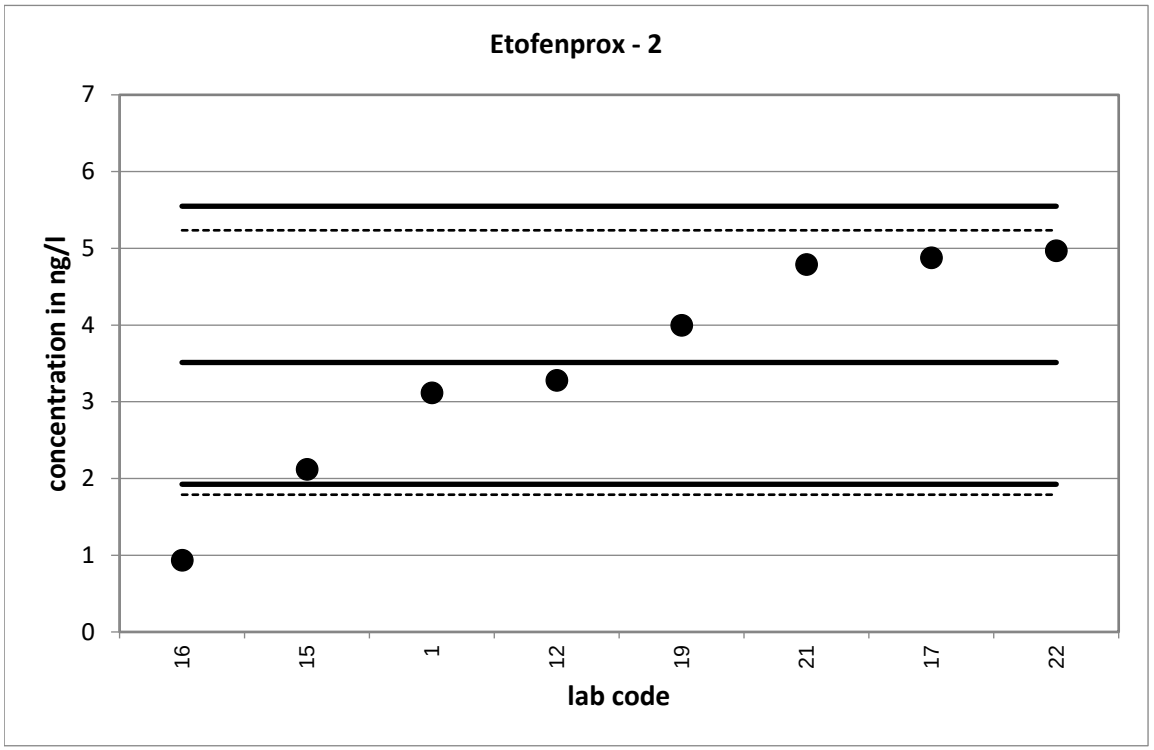
Strongly deviating values are not correctly shown in the diagram.



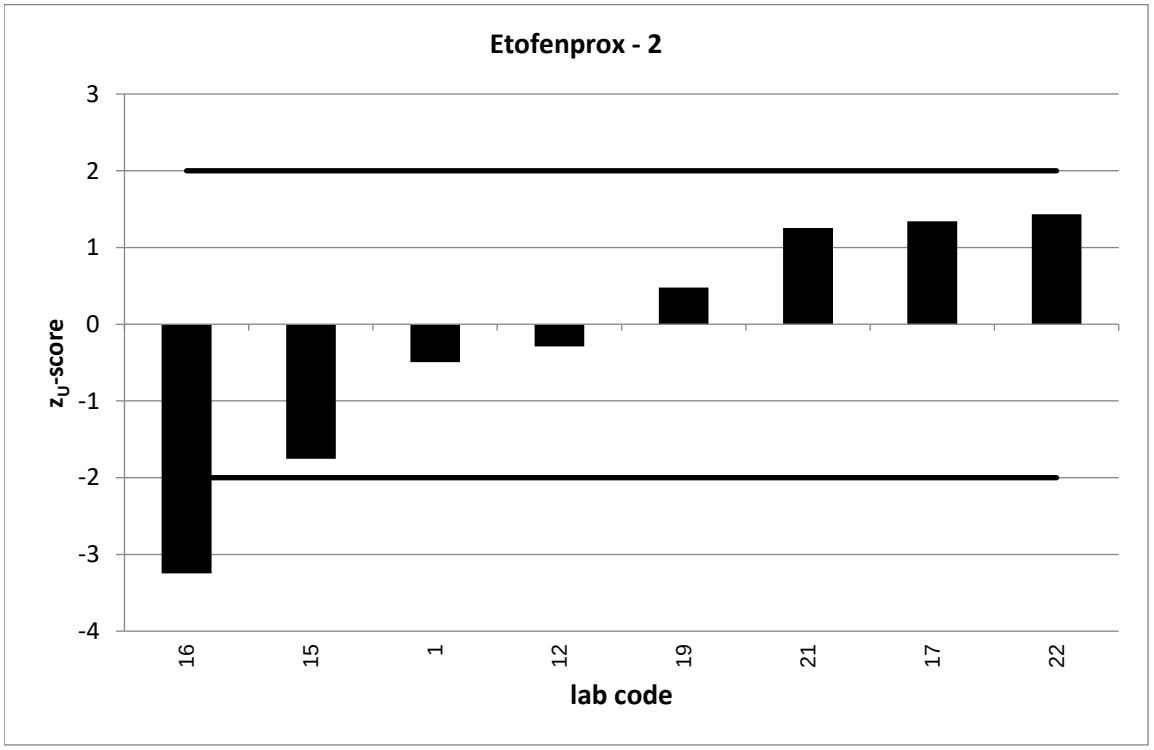
PT 4/24 - Pyrethroids		Etofenprox - 2			
assigned value [ng/l]*			3,512	± 1,723	
upper tolerance limit [ng/l]			5,548		
lower tolerance limit [ng/l]			1,925		
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	3,12	0,935	-0,4	-0,5	s
12	3,283	0,985	-0,2	-0,3	s
15	2,12	0,53	-1,5	-1,8	s
16	0,936	0,094	-3,0	-3,2	u
17	4,877	3,414	0,7	1,3	s
19	4	0,6	0,5	0,5	s
21	4,79	2,4	0,9	1,3	s
22	4,97	1,32	1,3	1,4	s

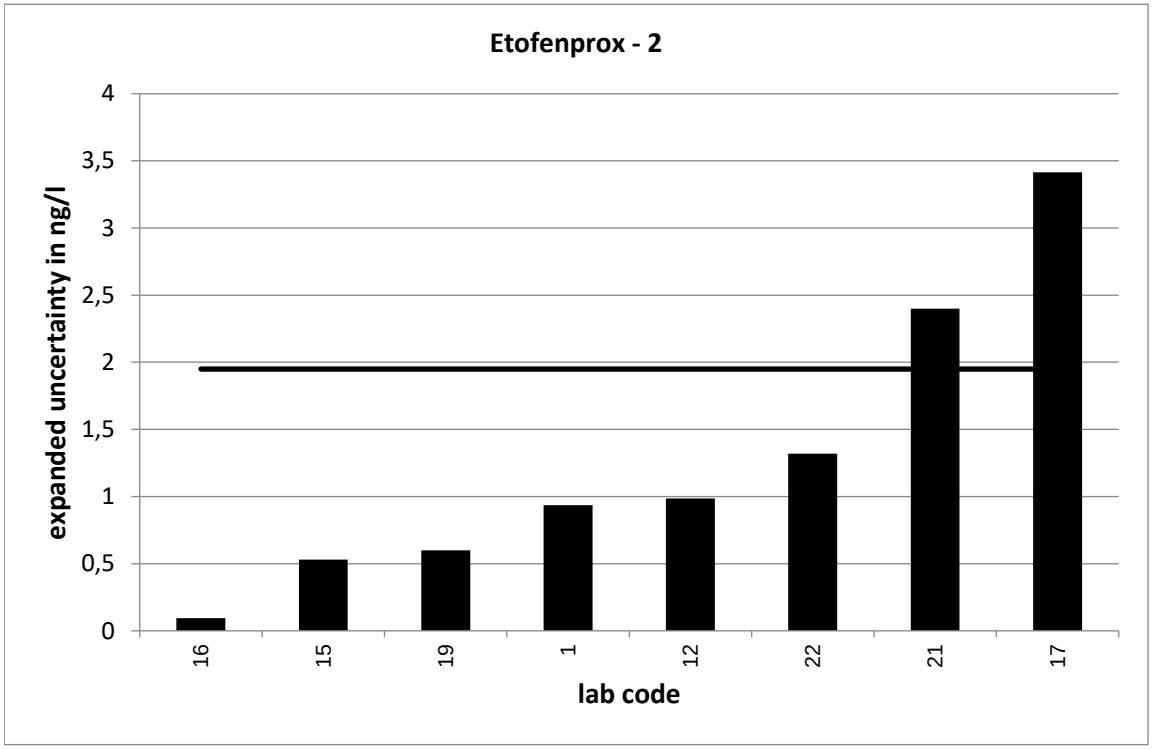
* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

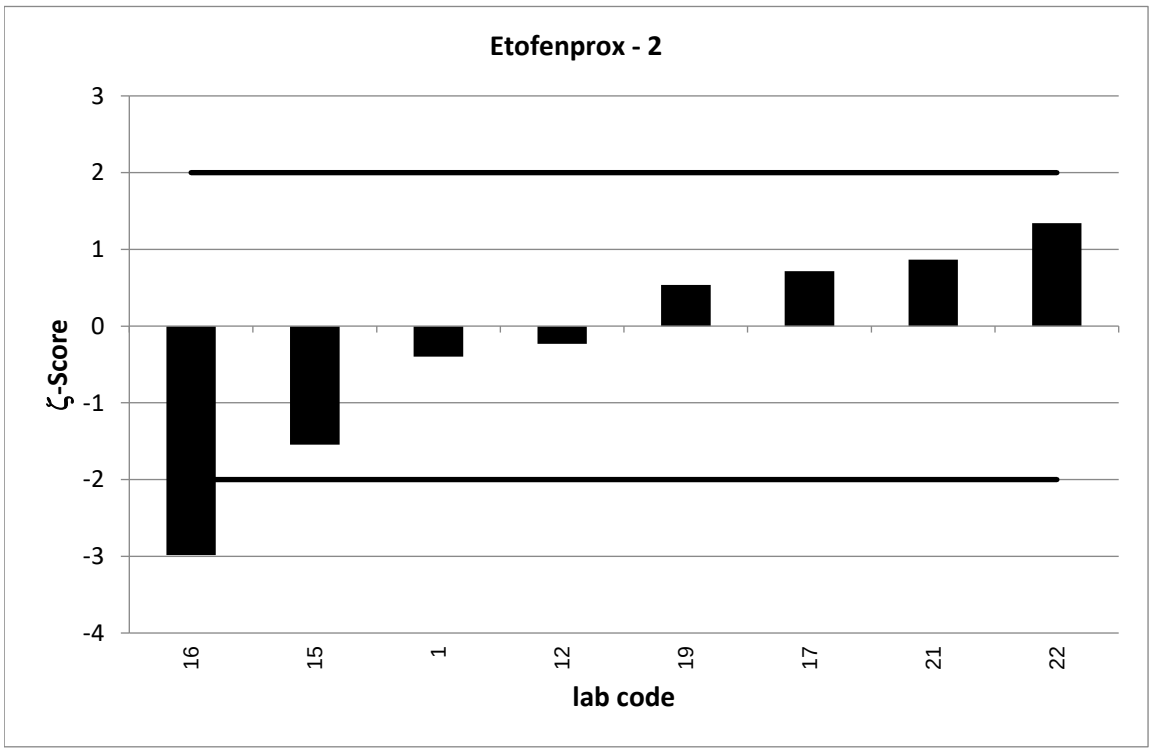
** s = satisfactory, q = questionable, u = unsatisfactory



Strongly deviating values are not shown in the diagram.



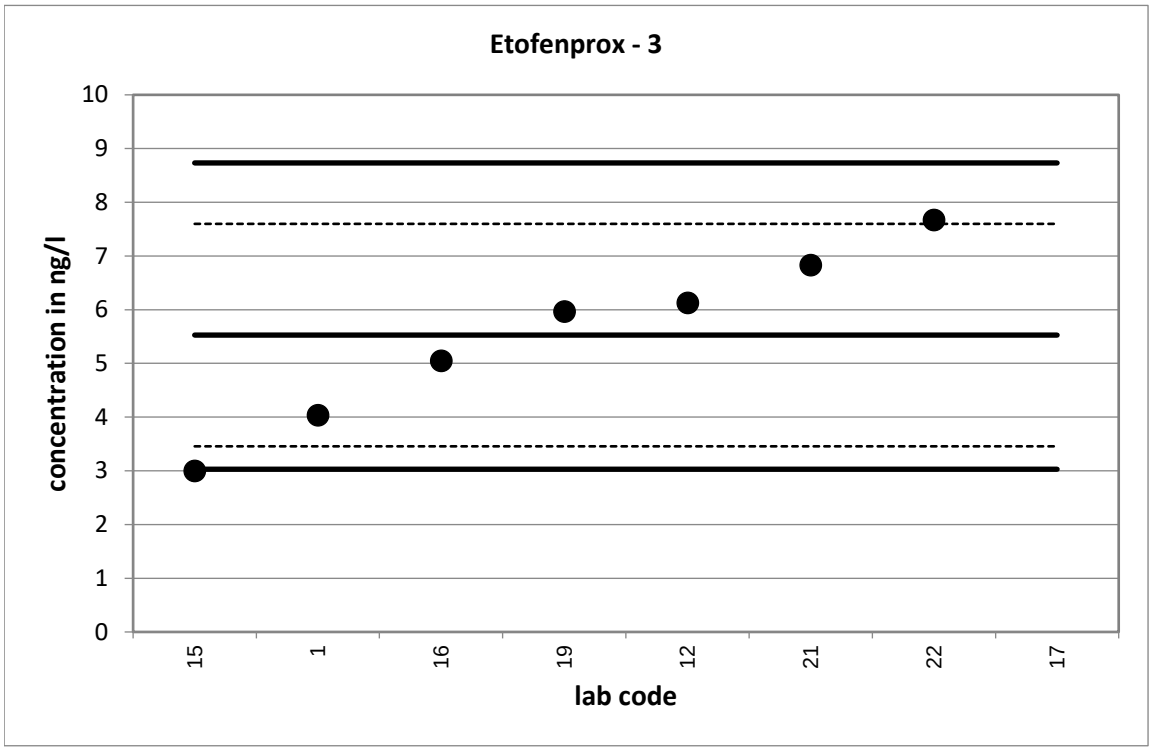

Etofenprox - 2
expanded uncertainty in ng/l
4
3,5
3
2,5
2
1,5
1
0,5
0
16
15
19
1
12
22
21
17
lab code


Etofenprox - 2
ζ-Score
3
2
1
0
-1
-2
-3
-4
16
15
1
12
19
17
21
22
lab code

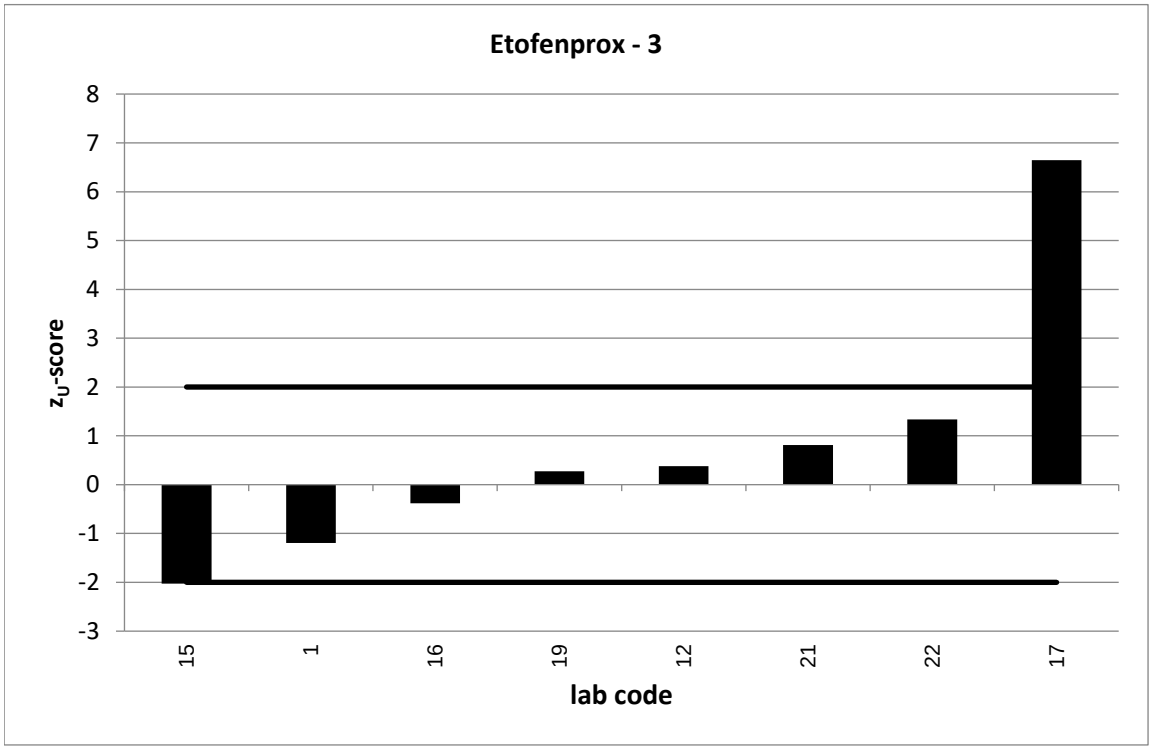
PT 4/24 - Pyrethroids		Etofenprox - 3			
assigned value [ng/l]*			5,527	± 2,071	
upper tolerance limit [ng/l]			8,732		
lower tolerance limit [ng/l]			3,03		
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	4,04	1,21	-1,2	-1,2	s
12	6,132	1,839	0,4	0,4	s
15	2,999	0,75	-2,3	-2,0	s
16	5,05	0,504	-0,4	-0,4	s
17	16,177	11,32	1,9	6,6	u
19	5,97	0,896	0,4	0,3	s
21	6,83	3,42	0,7	0,8	s
22	7,67	2,04	1,5	1,3	s

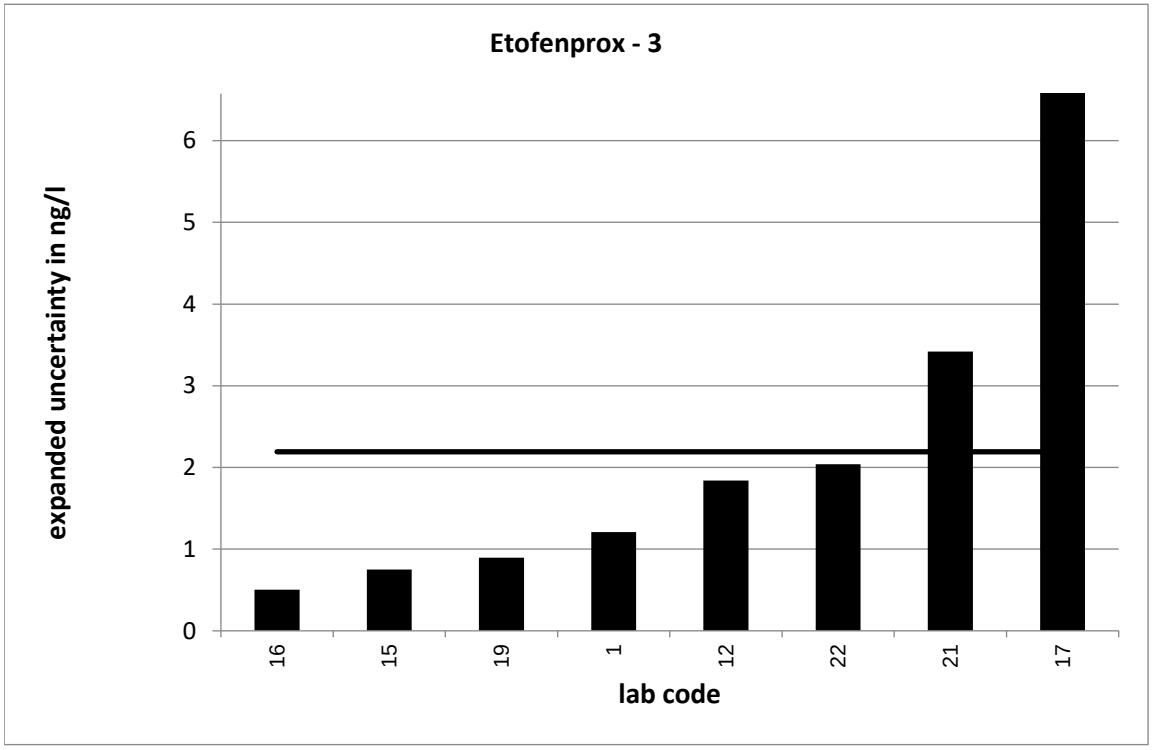
* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

** s = satisfactory, q = questionable, u = unsatisfactory

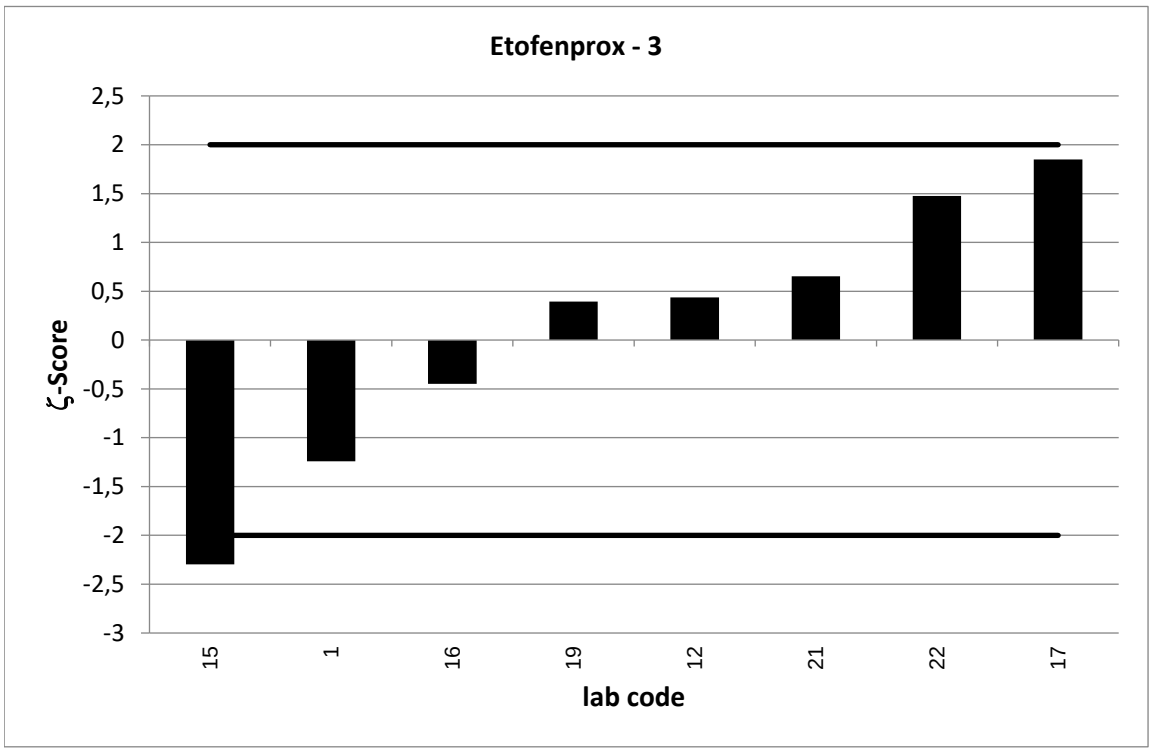


Strongly deviating values are not shown in the diagram.



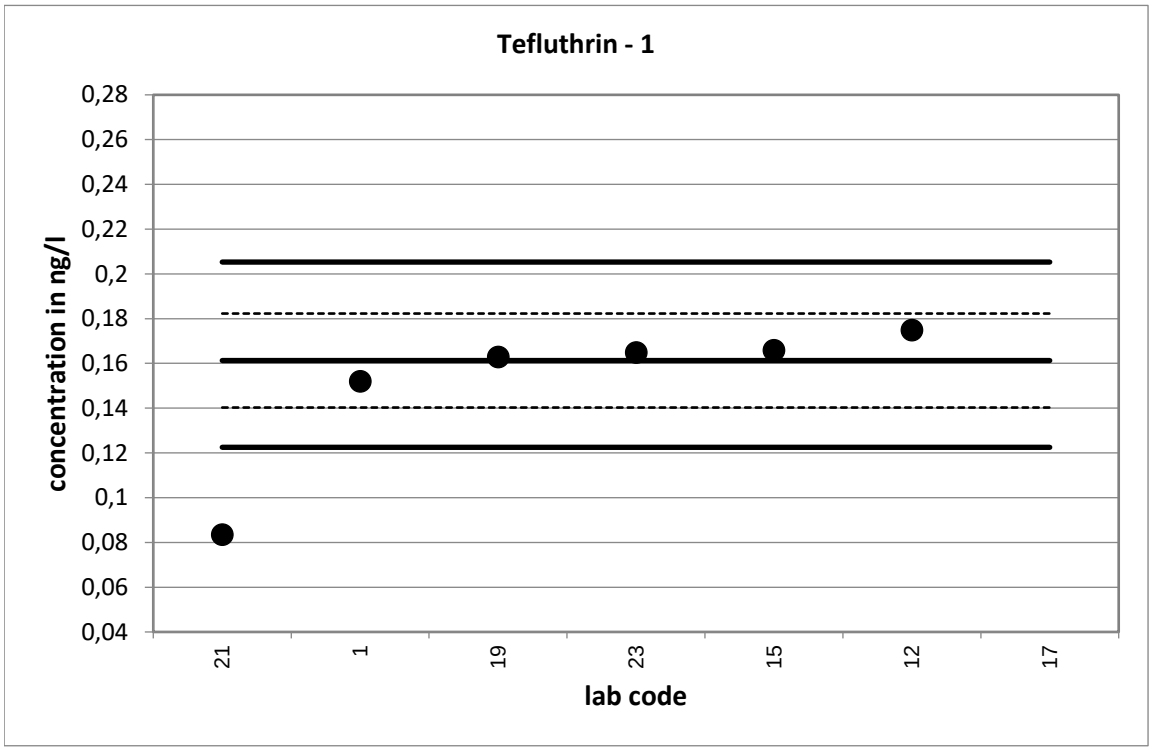


Strongly deviating values are not correctly shown in the diagram.

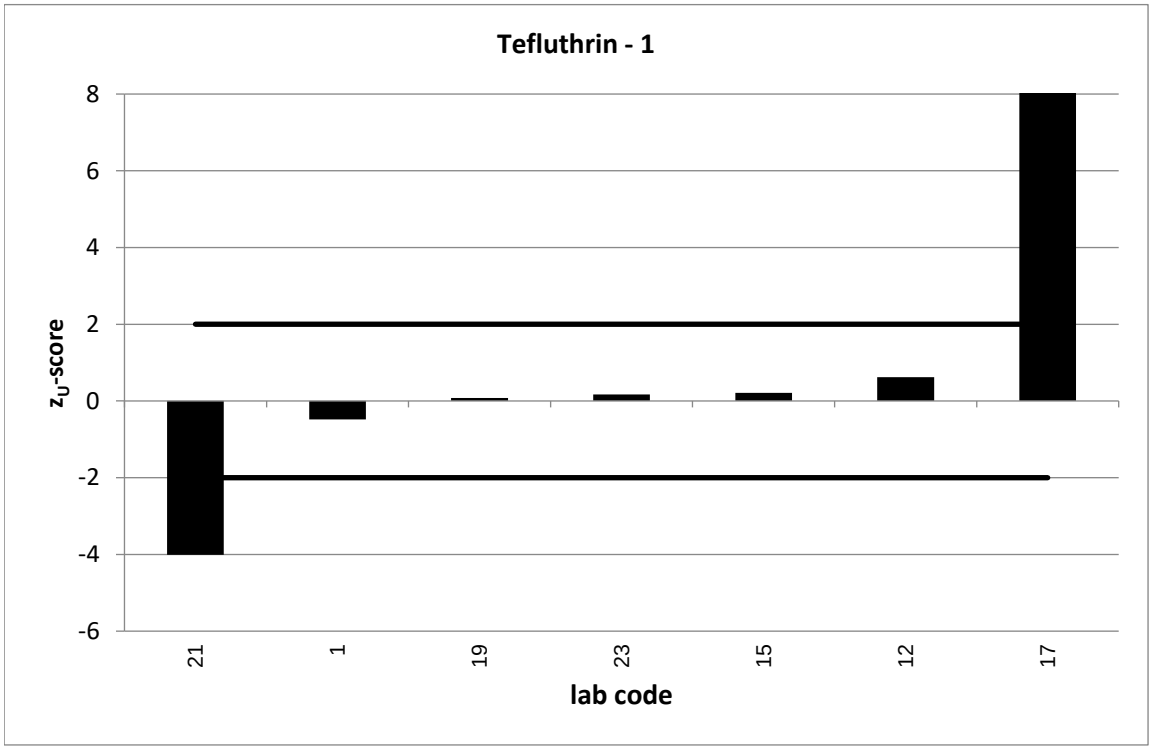


PT 4/24 - Pyrethroids		Tefluthrin - 1			
assigned value [ng/l]*			0,1613	± 0,021	
upper tolerance limit [ng/l]			0,2053		
lower tolerance limit [ng/l]			0,1225		
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,152	0,046	-0,4	-0,5	s
12	0,175	0,053	0,5	0,6	s
15	0,166	0,033	0,2	0,2	s
17	1,119	0,783	2,4	43,5	u
19	0,163	0,024	0,1	0,1	s
21	0,0835	0,042	-3,3	-4,0	u
23	0,165	0,018	0,3	0,2	s

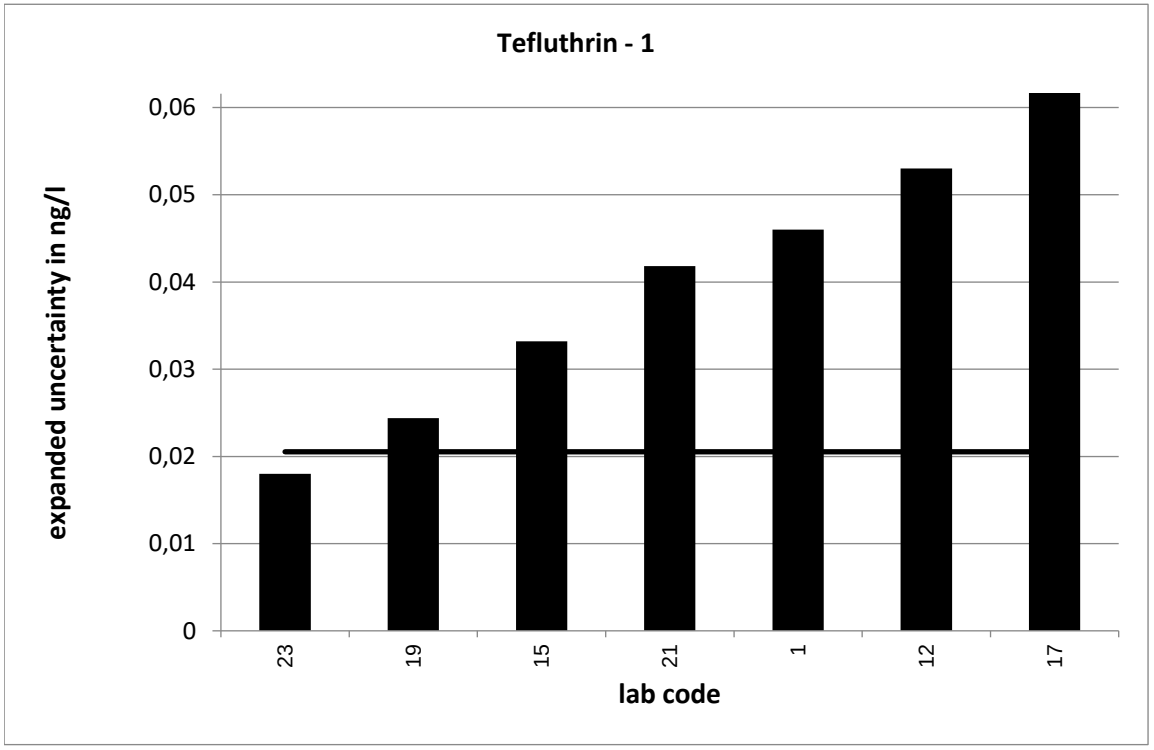
* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%
** s = satisfactory, q = questionable, u = unsatisfactory



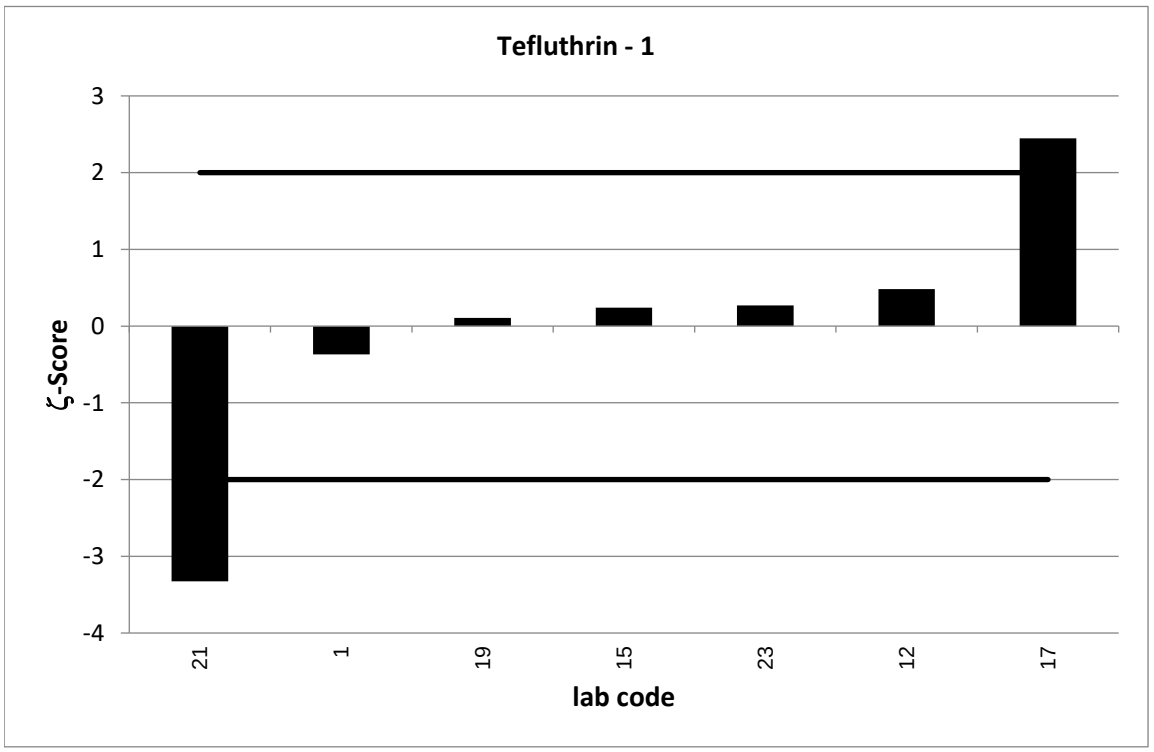
Strongly deviating values are not shown in the diagram.



Strongly deviating values are not correctly shown in the diagram.

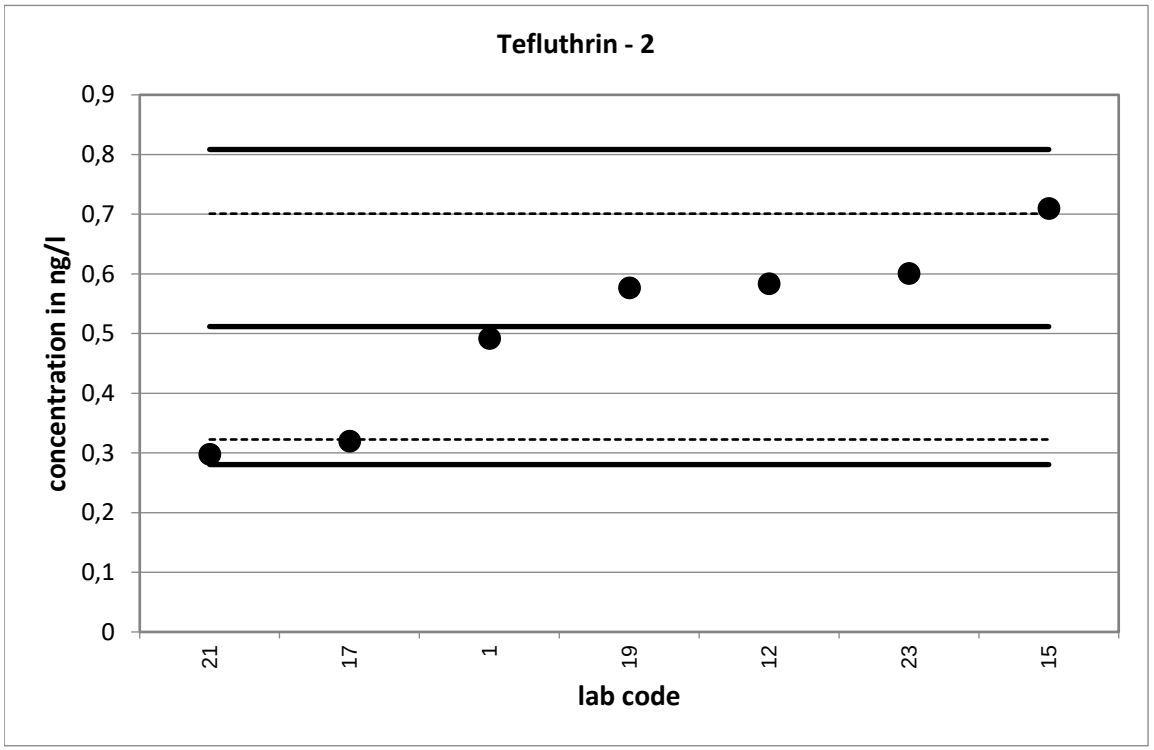


Strongly deviating values are not correctly shown in the diagram.

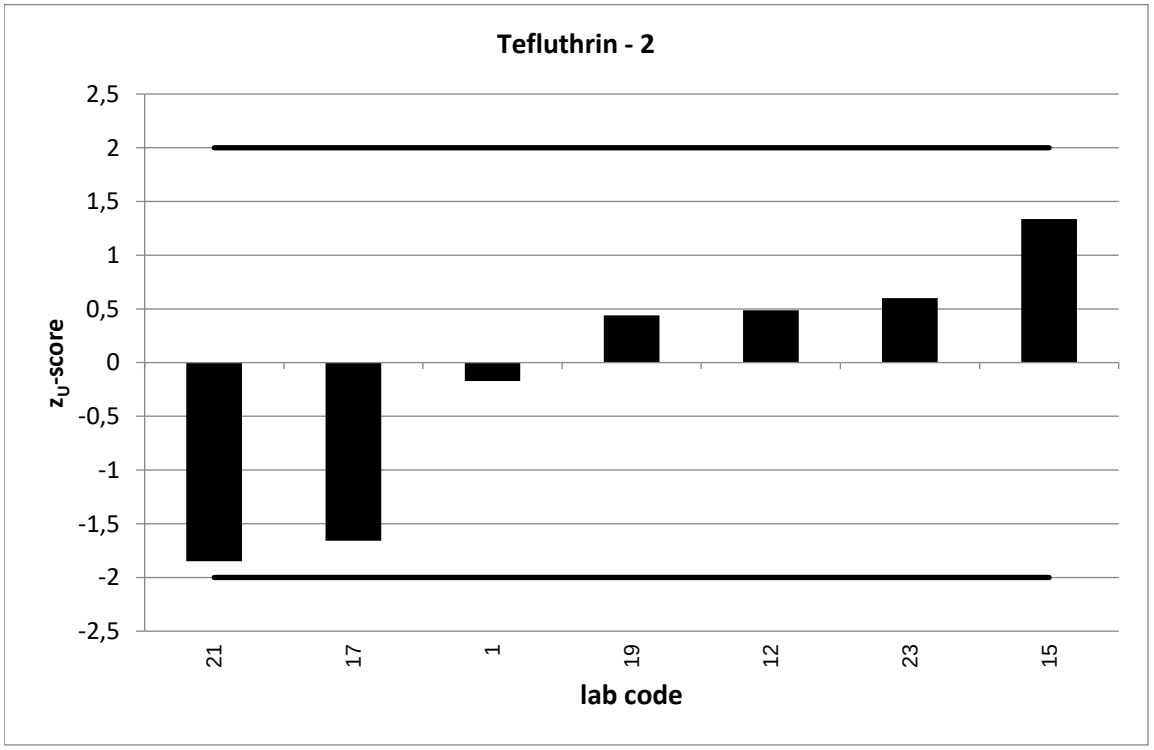


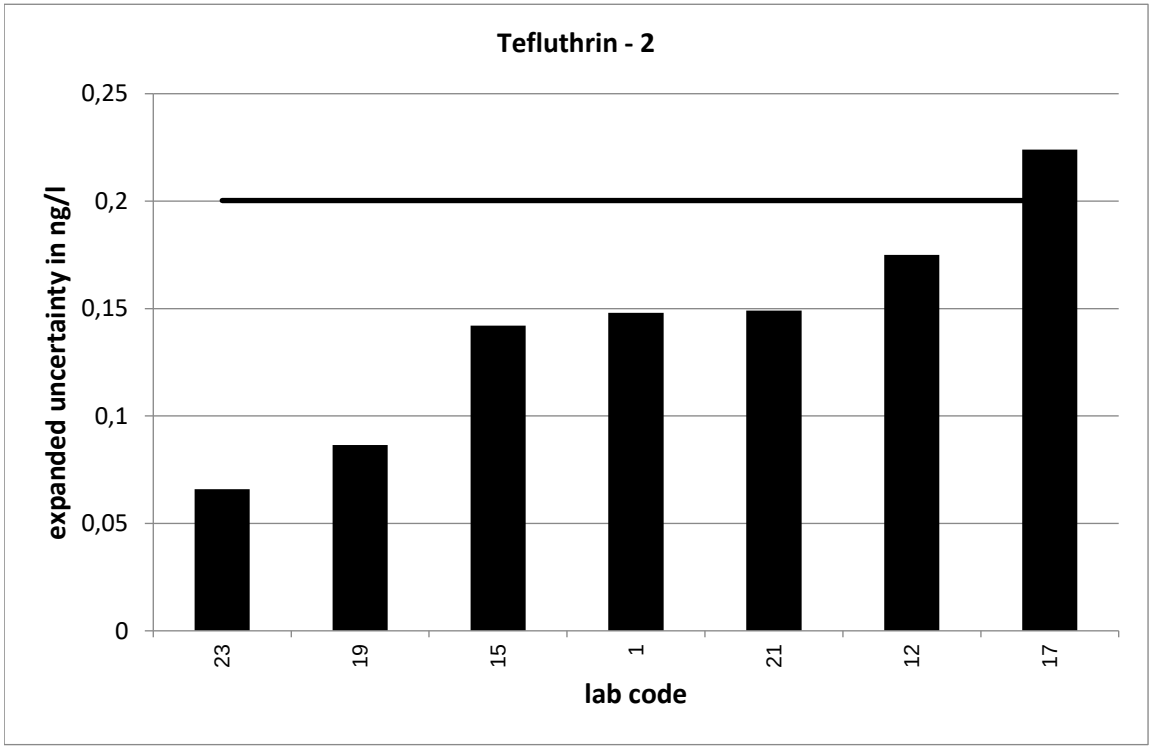
PT 4/24 - Pyrethroids		Tefluthrin - 2			
assigned value [ng/l]*			0,5117	± 0,1892	
upper tolerance limit [ng/l]			0,8084		
lower tolerance limit [ng/l]			0,2805		
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	0,492	0,148	-0,2	-0,2	s
12	0,584	0,175	0,6	0,5	s
15	0,71	0,142	1,7	1,3	s
17	0,32	0,224	-1,3	-1,7	s
19	0,577	0,087	0,6	0,4	s
21	0,298	0,149	-1,8	-1,8	s
23	0,601	0,066	0,9	0,6	s

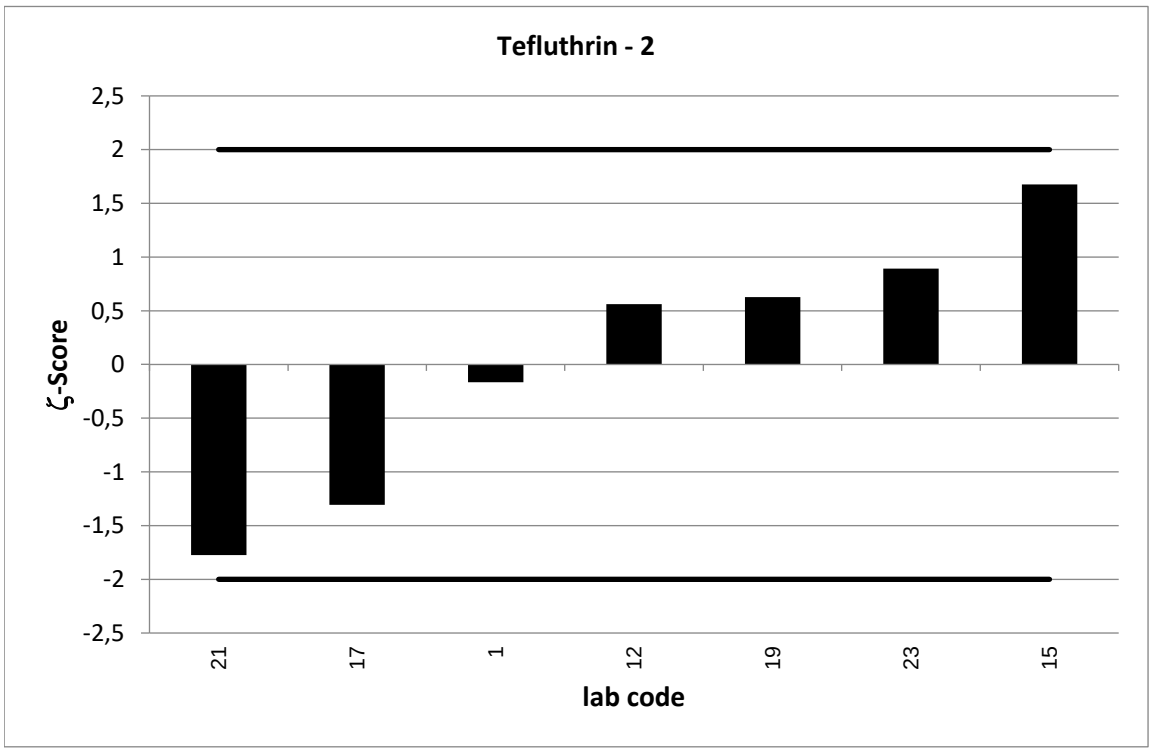
* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%
** s = satisfactory, q = questionable, u = unsatisfactory



Strongly deviating values are not shown in the diagram.

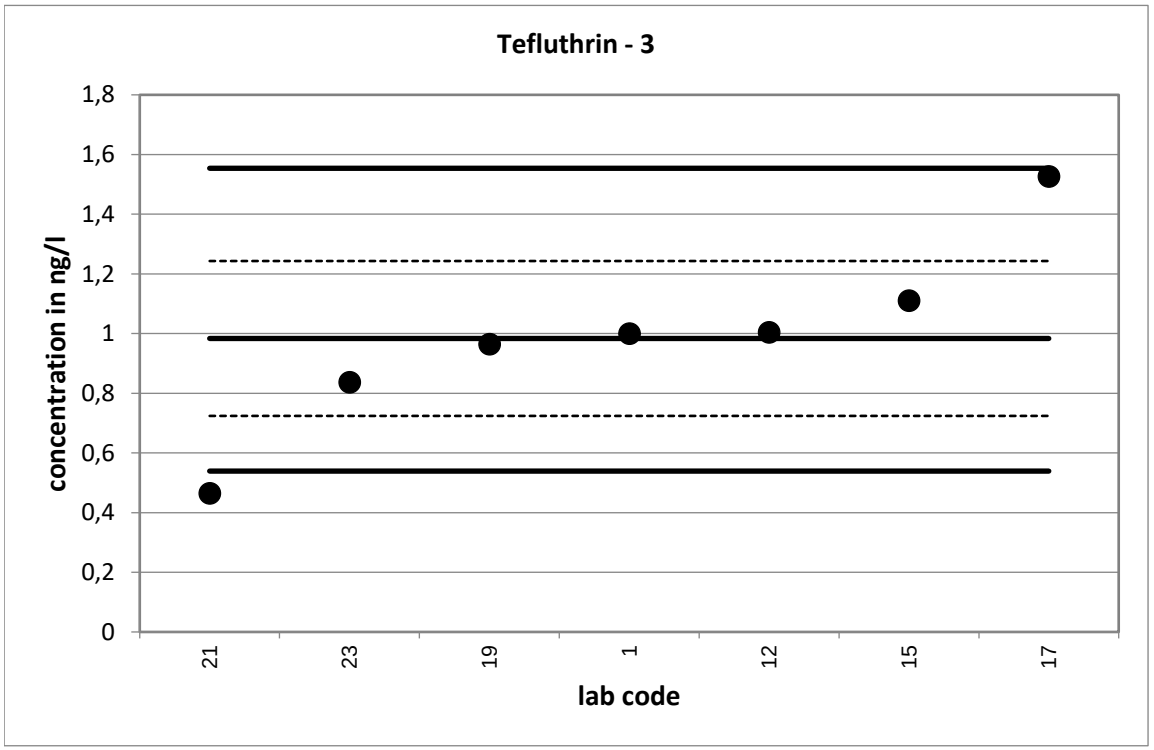



Tefluthrin - 2
expanded uncertainty in ng/l
0,25
0,2
0,15
0,1
0,05
0
23
19
15
1
21
12
17
lab code

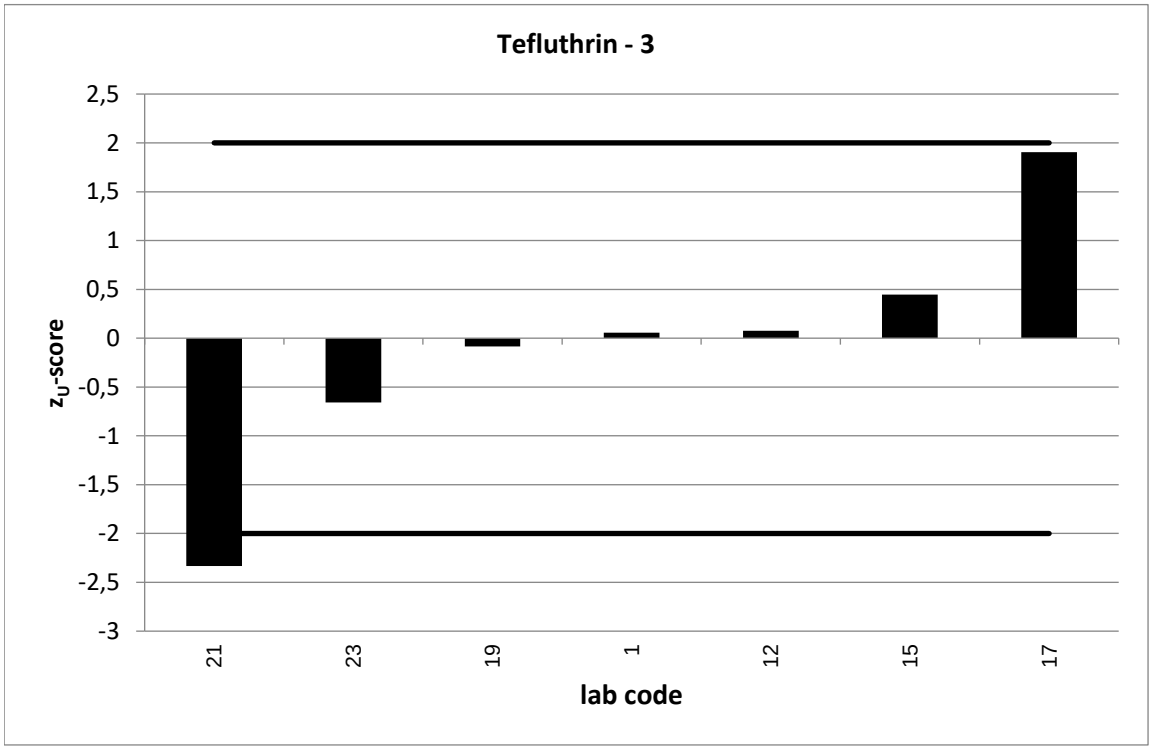

Tefluthrin - 2
ζ-Score
2,5
2
1,5
1
0,5
0
-0,5
-1
-1,5
-2
-2,5
21
17
1
12
19
23
15
lab code

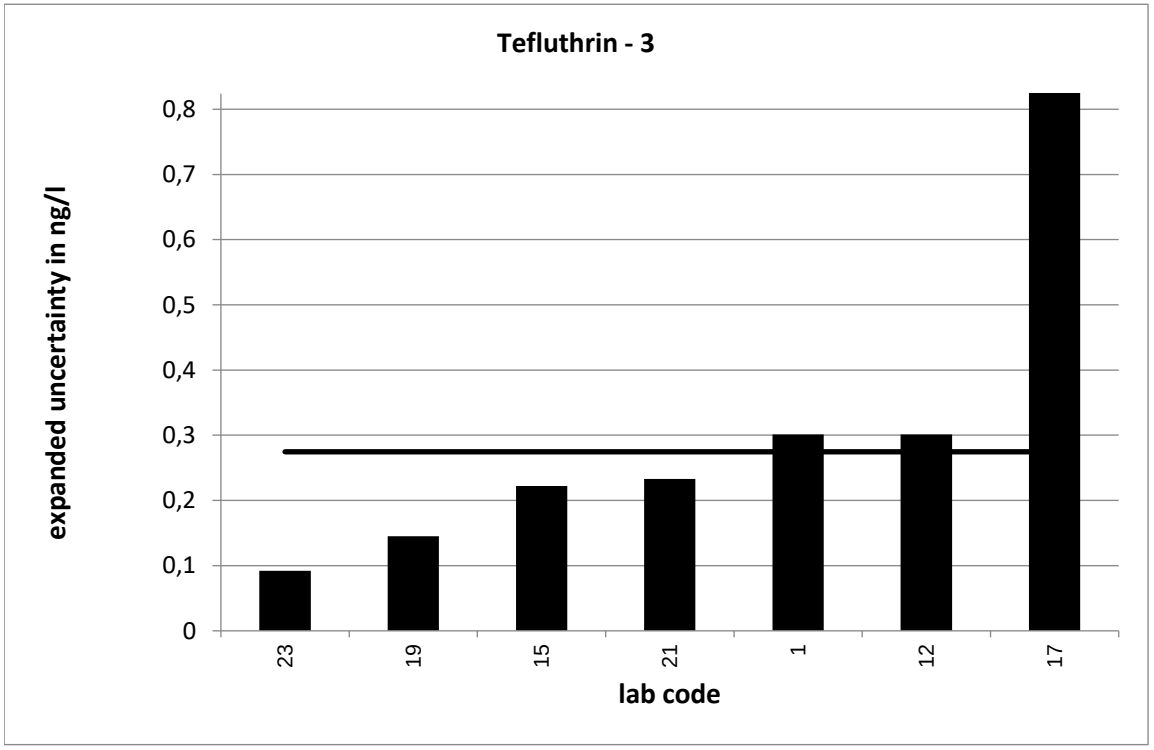
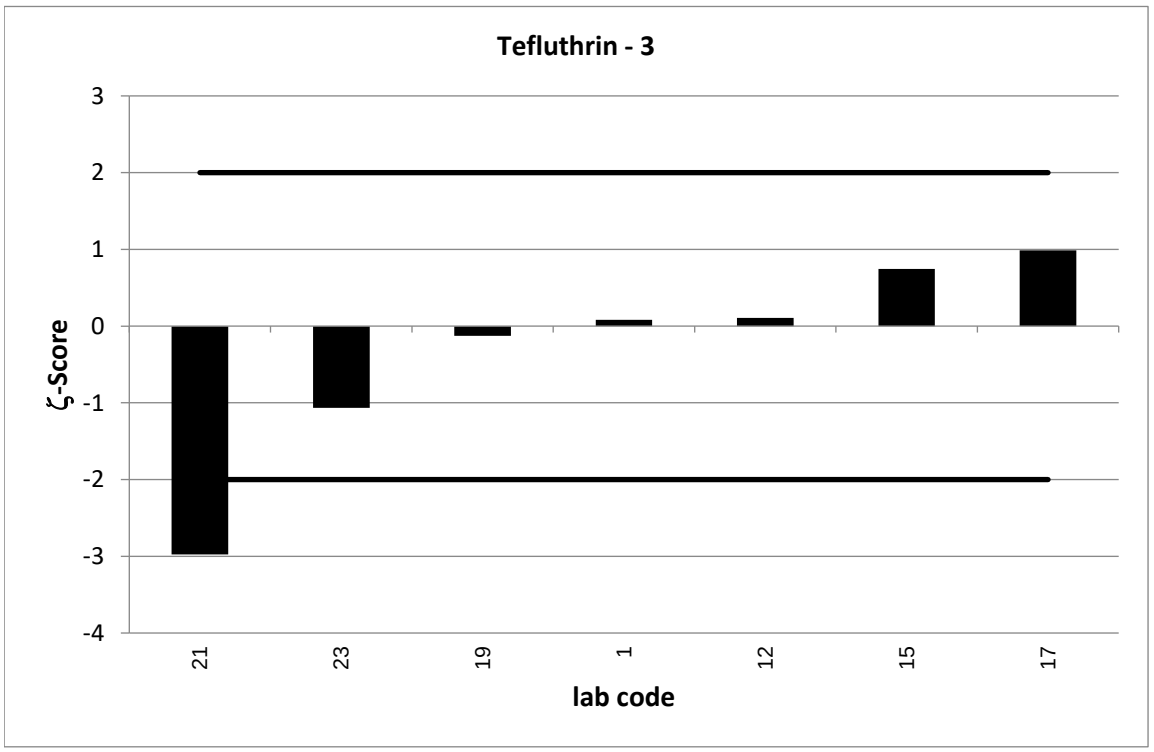
PT 4/24 - Pyrethroids		Tefluthrin - 3			
assigned value [ng/l]*			0,9836	± 0,2595	
upper tolerance limit [ng/l]			1,554		
lower tolerance limit [ng/l]			0,5391		
lab code	result [ng/l]	±	z-score	z_U-score	assessm.**
1	1	0,301	0,1	0,1	s
12	1,005	0,301	0,1	0,1	s
15	1,111	0,222	0,7	0,4	s
17	1,527	1,069	1,0	1,9	s
19	0,965	0,145	-0,1	-0,1	s
21	0,465	0,233	-3,0	-2,3	q
23	0,837	0,092	-1,1	-0,7	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%
** s = satisfactory, q = questionable, u = unsatisfactory



Strongly deviating values are not shown in the diagram.





Strongly deviating values are not correctly shown in the diagram.