Analytische Qualitätssicherung Baden-Württemberg

Proficiency Tests UKWIR 13/20 and 14/20 priority substances in surface water -

Triclosan and tributyltin

Stuttgart, January 2021

provided by

AQS Baden-Württemberg

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University of Stuttgart

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General

This PT was provided by AQS Baden-Württemberg as a subcontractor for wca environment limited, Brunel House, Volunteer Way, Faringdon, Oxfordshire SN7 7YR, United Kingdom on behalf of United Kingdom Water Industry Research (UKWIR).

In the PT rounds reported here the following determinands were to be measured:

- UKWIR 13/20: triclosan
- UKWIR 14/20: tributyltin

The PTs were executed and evaluated according to the requirements of ISO 13528: 2015.

PT design

Each participant received the following samples for the PT rounds UKWIR 13/20 and 14/20:

- 3 spiked samples for the determination of the respective determinands based on
  - filtered surface for triclosan in PT UKWIR 13/20 and
  - drinking water for tributyltin in PT UKWIR 14/20

  in 1000 ml glass bottles with ground glass plug
- 1 blank sample of the surface and drinking water resp.

The concentrations of the analytes of the spiked samples were chosen according to the requirements of UKWIR based on the European Regulation for Environmental Quality Standard (Directive 2008/105/EG on environmental quality standards in the field of water policy).

The samples were cooled directly after preparation and dispatched with freezer packs added to the packages by express service (GO! Express). Participants were requested to start with the analysis one day after receipt of the samples at the latest.

Analytical methods

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

Determinand	Required LOQ in ng/l
triclosan	10
tributyltin	0.12

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

Evaluation procedure

The statistical evaluation was executed according to ISO 13528:2015 with the combined estimator Hampel/Q-method, a method of robust statistics.

The uncertainty of the assigned value was calculated acccording to ISO 13528:

$$u(x_{pt}) = \frac{1,25 \; x \; s^*}{\sqrt{p}}$$

s*: standard deviation calculated from the results using the Q-method
p: number of results

The standard deviation for proficiency assessment σ_{pt} was calculated in accordance with the European QA/QC Directive: $\sigma_{pt} = 0,25 * x_{pt}$.

A z-score was calculated for each measurement result derived from the assigned value x_{pt} and the standard deviation for proficiency assessment σ_{pt}:

$$z = \frac{x - x_{pt}}{\sigma_{pt}}$$

The assessment of the results was as follows:
$|z| \leq 2.0$ satisfactory
$2.0 < |z| < 3.0$ questionable
$|z| \geq 3.0$ unsatisfactory

Results of evaluation

Number of participants:

PT round	determinands	number of participants	number of participants reporting results
UKWIR 13/20	triclosan	10	9
UKWIR 14/20	tributyltin	10	10

In the following figure the percentage of satisfactory, questionable and unsatisfactory results are illustrated.
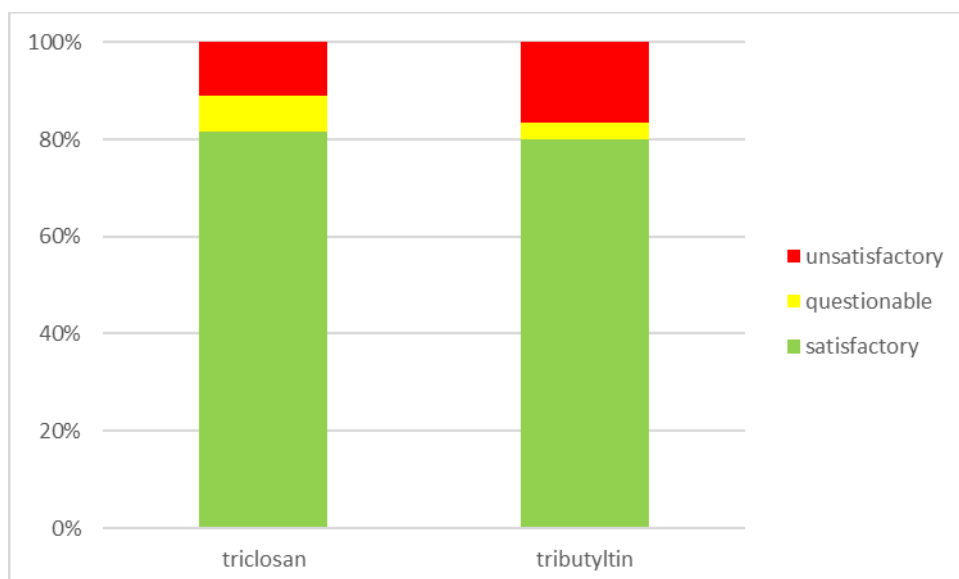
Explanation of tables and graphs in the appendix

The appendix contains the PT data for all parameters and all samples in tables and graphs. For each parameter the following illustrations are given:

Parameter table

In these tables the following values for each concentration level are listed:
- assigned value in ng/l
- expanded uncertainty of the assigned value in %
- standard deviation of the data set in ng/l, calculated using the Q-method (due to the often low number of participants this standard deviation estimate is not very reliable)
- standard deviation for proficiency assessment in ng/l for the calculation of z-scores (25 % of the assigned value)
- rel. standard deviation for proficiency assessment in %
- tolerance limits above and below in ng/l and % (limit for assessment as 'satisfactory')
- number of values in this level
- number of not satisfactory values ('questionable' or unsatisfactory') below and above the assigned value and the percentage of these values in total

Relative standard deviation

The diagrams for the rel. standard deviation vs. the assigned value show the values compared to the fixed standard deviation for proficiency assessment (horizontal line at 25%) and the concentration dependence.

Sample table

In this table all results of the participants are noted together with uncertainties (where reported). For these uncertainties ζ-scores (zeta-scores) are calculated according to the formula

$$\zeta = \frac{x - x_{pt}}{\sqrt{u_{lab}^2 + u_{x_{pt}}^2}}$$

With

x = result of the participant
x_{pt} = assigned value
u_{lab} = participant's standard uncertainty
$u_{x,pt}$ = standard uncertainty of the assigned value

ζ-scores can be used for the plausibility check of measurement uncertainties. The type of assessment is equivalent to that of z-scores, i.e. an absolute value of ≤ 2,0 can be regarded as 'satisfactory'.
ζ-scores above this value indicate an underestimation of the measurement uncertainty. This table also contains the assigned value and its uncertainty as well as the tolerance limits (z = ± 2,0).

Sample graphs of concentrations

All participants' results, sorted for values, are shown here versus the laboratory codes. The assigned value and its uncertainty as well as the tolerance limits are also included.

z-score graphs

In a similar way the z-scores attributed to the participants' results are shown here versus the laboratory codes.

Graphs of expanded uncertainty

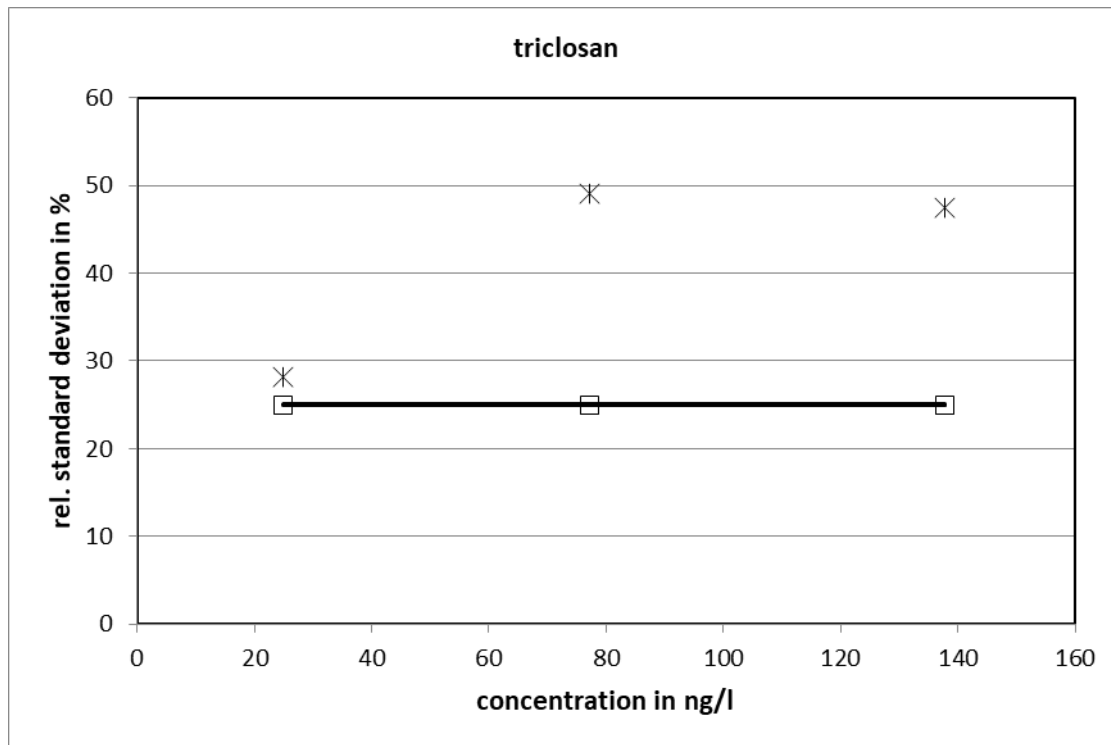The expanded uncertainty is shown if laboratories reported uncertainties.

ζ-score graphs

If laboratories reported uncertainties, ζ-scores were calculated and are shown versus the laboratory codes.

UKWIR 13/20

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 [%]
					triclosan								
1	24,96	23,47	7,030	6,240	25	39,43	13,68	57,99	-45,19	9	0	1	11,1
2	77,08	40,90	37,83	19,27	25	121,8	42,25	57,99	-45,19	9	1	1	22,2
3	137,7	39,56	65,35	34,42	25	217,5	75,47	57,99	-45,19	9	1	1	22,2
									sum	27	2	3	18,5

Relative standard deviation

triclosan

25 % is the value used as standard deviation for proficiency assessment.

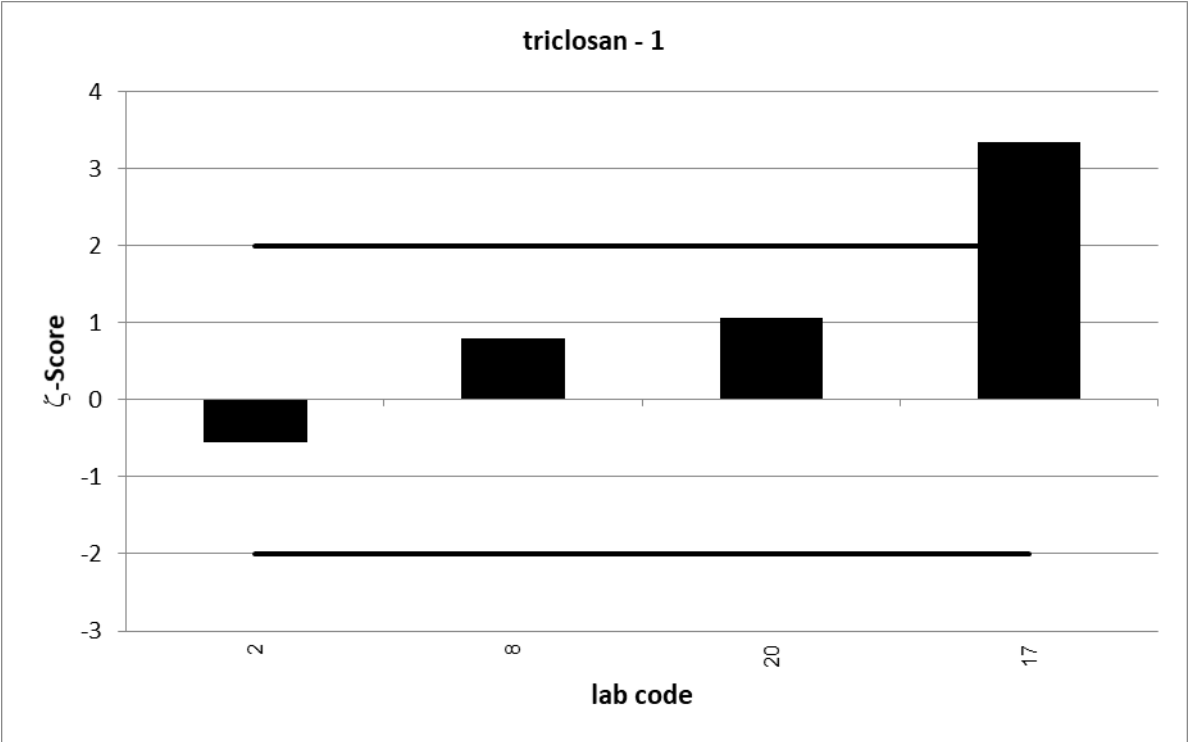AQS Baden-Württemberg

UKWIR PT 13/20	triclosan - 1				
assigned value [ng/l]*		24,96	± 5,86		
upper tolerance limit [ng/l]		39,43			
lower tolerance limit [ng/l]		13,68			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.**
2	21,6	10,8	-0,5	-0,6	s
3	32			1,0	s
4	20			-0,9	s
8	28,8	7,78	0,8	0,5	s
11	21			-0,7	s
13	16,864			-1,4	s
14	30			0,7	s
17	79,4	32	3,3	7,5	u
20	29,4	5,87	1,1	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

triclosan - 1

triclosan - 1
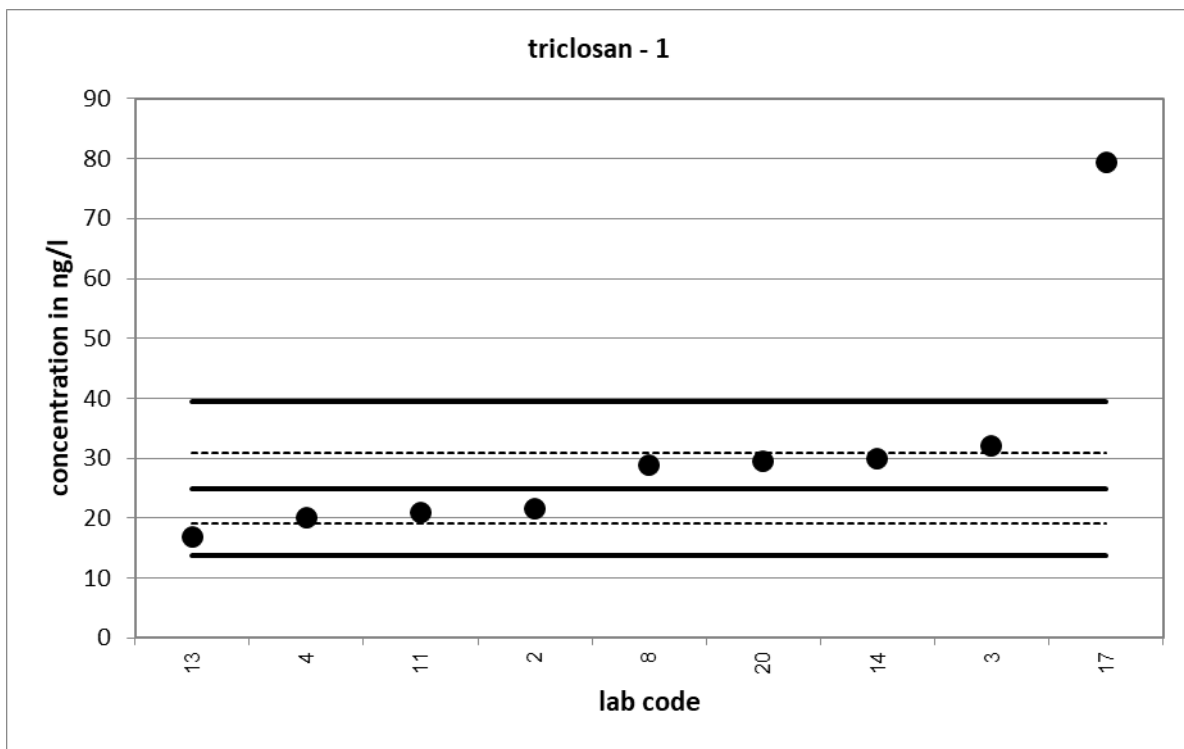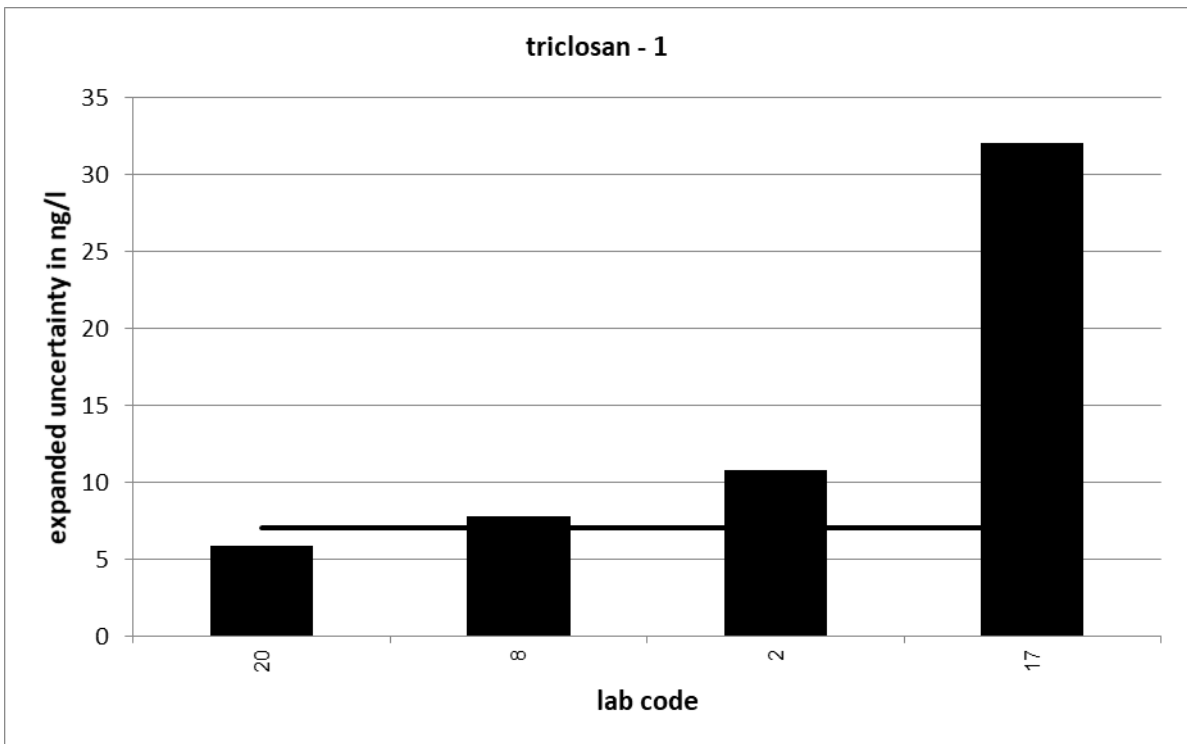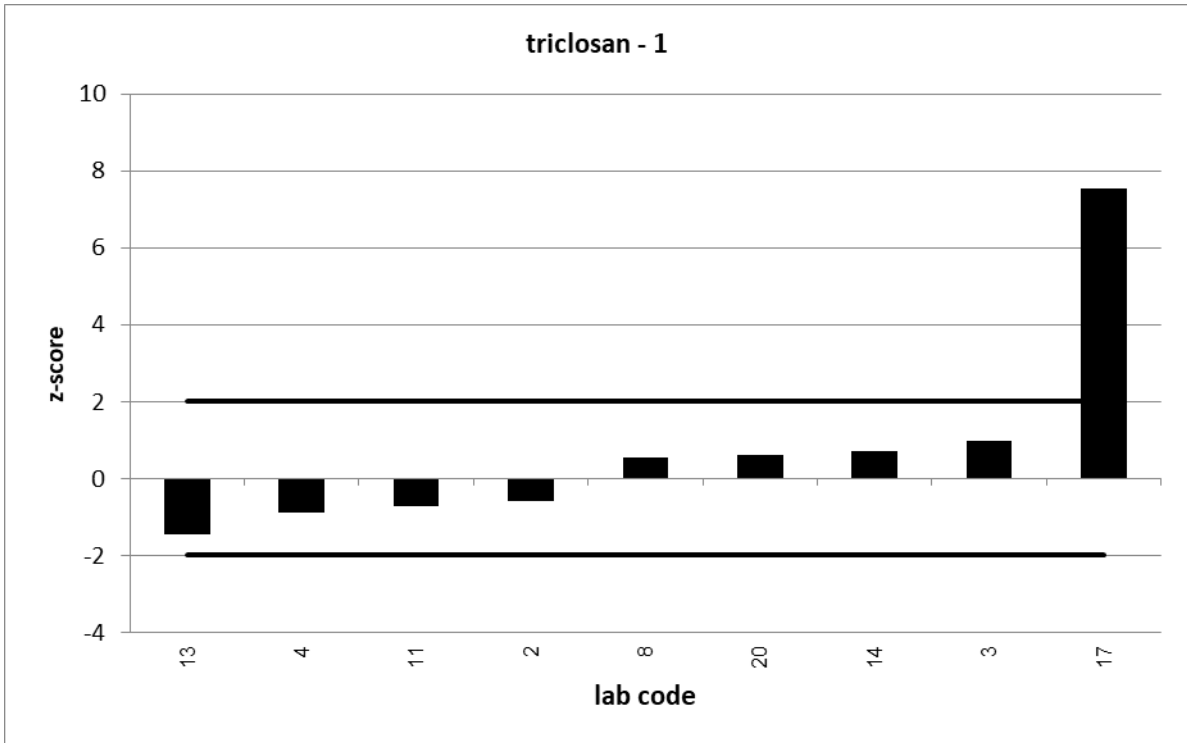
triclosan - 1

UKWIR PT 13/20	triclosan - 2				
assigned value [ng/l]*		77,08	± 31,53		
upper tolerance limit [ng/l]		121,8			
lower tolerance limit [ng/l]		42,25			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.**
2	74,6	37,3	-0,1	-0,1	s
3	98			0,9	s
4	70			-0,4	s
8	93,5	25,2	0,8	0,7	s
11	41			-2,1	q
13	64,1884			-0,7	s
14	70			-0,4	s
17	235	94	3,2	7,1	u
20	93	18,6	0,9	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%
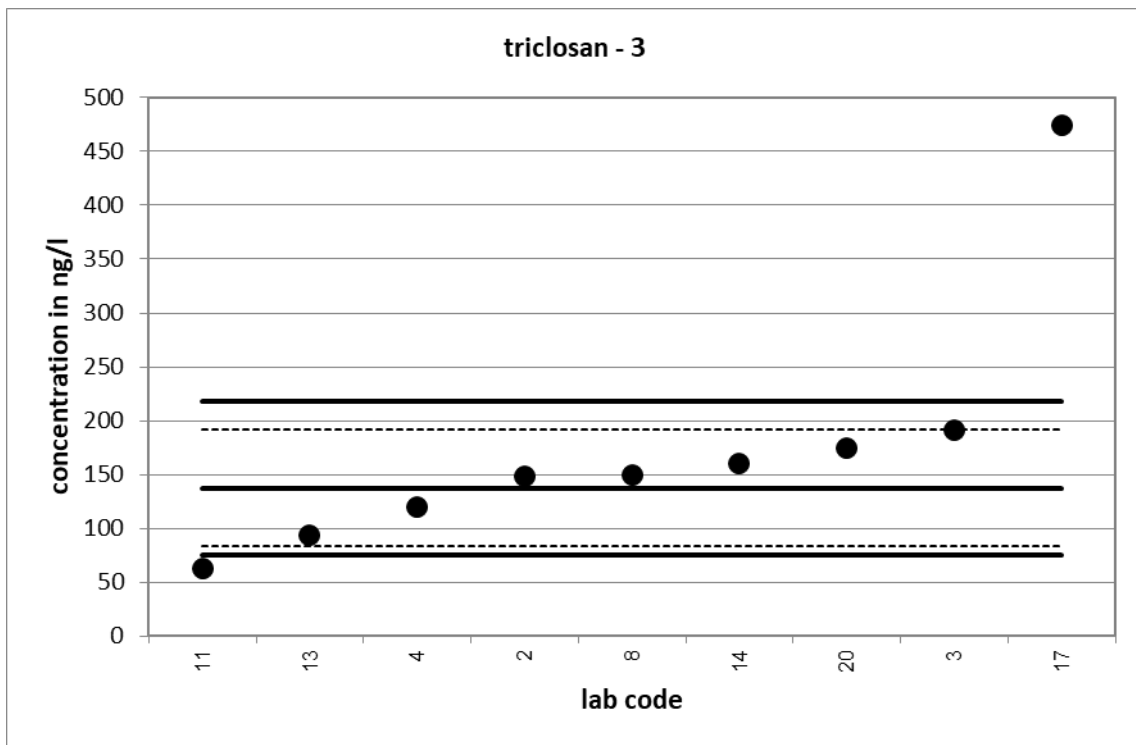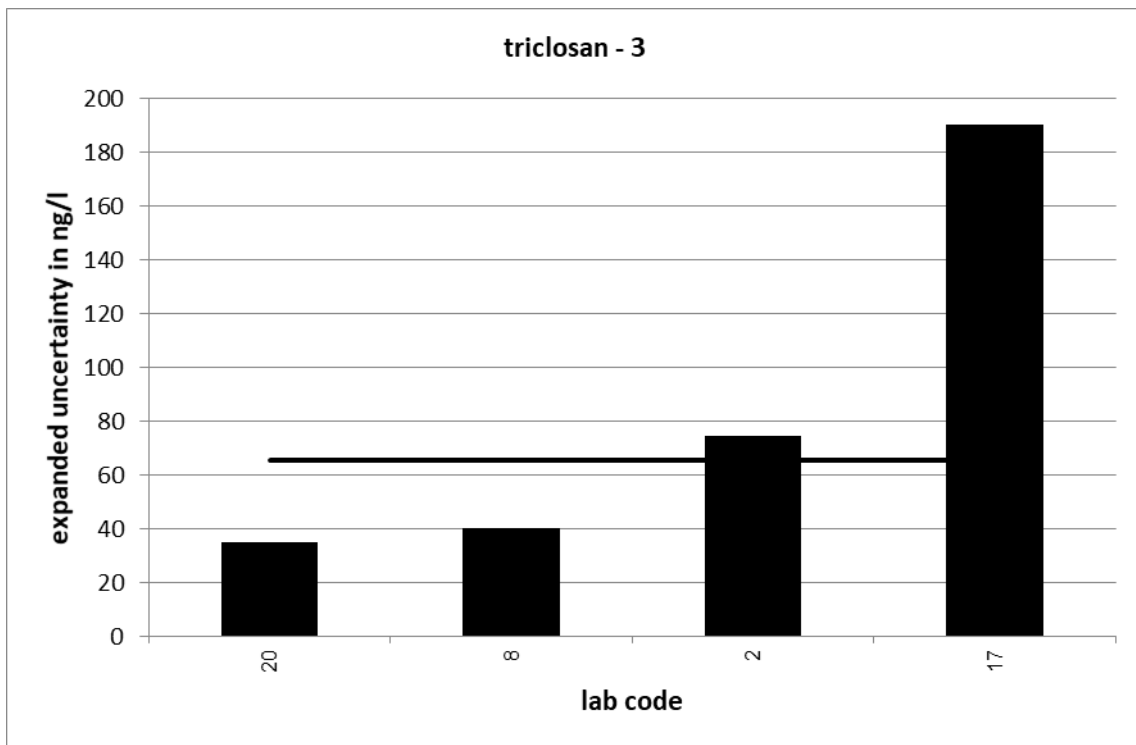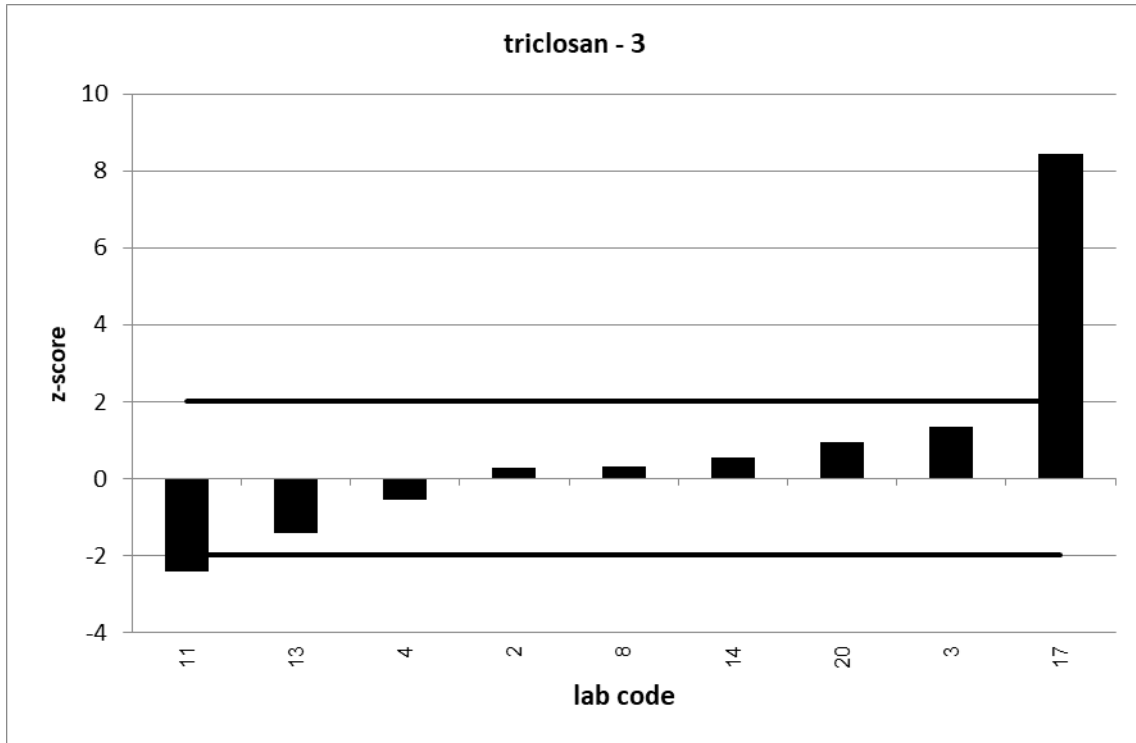** s = satisfactory, q = questionable, u = unsatisfactory

triclosan - 2
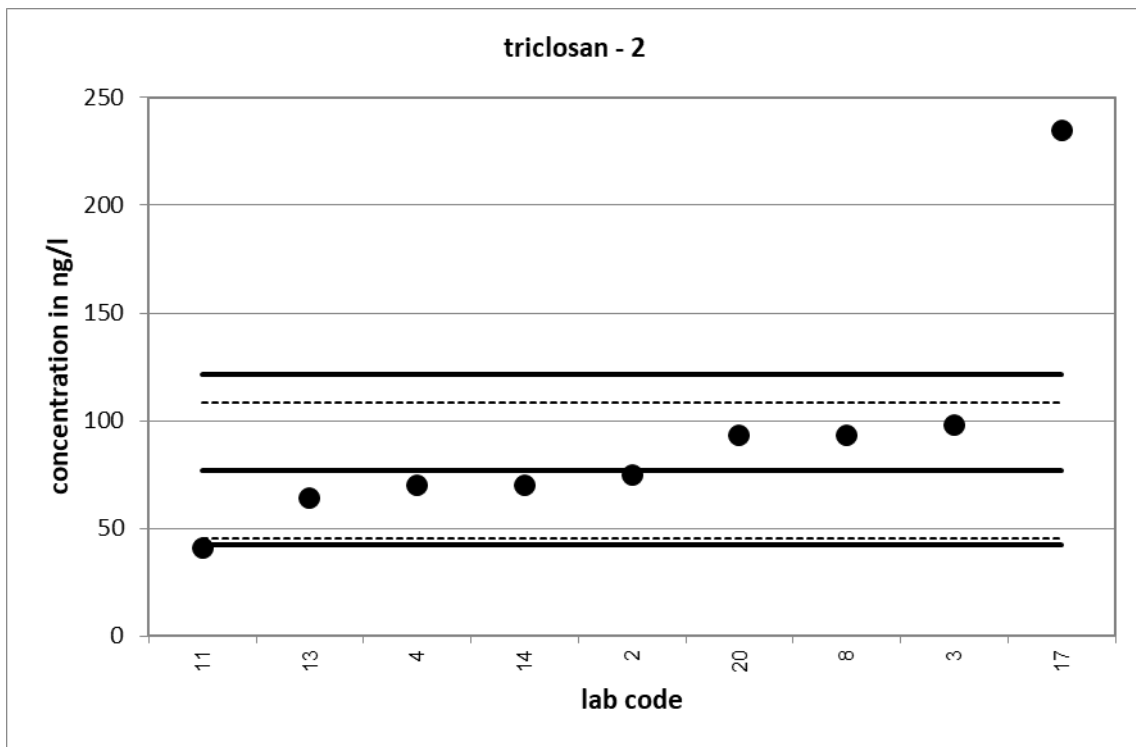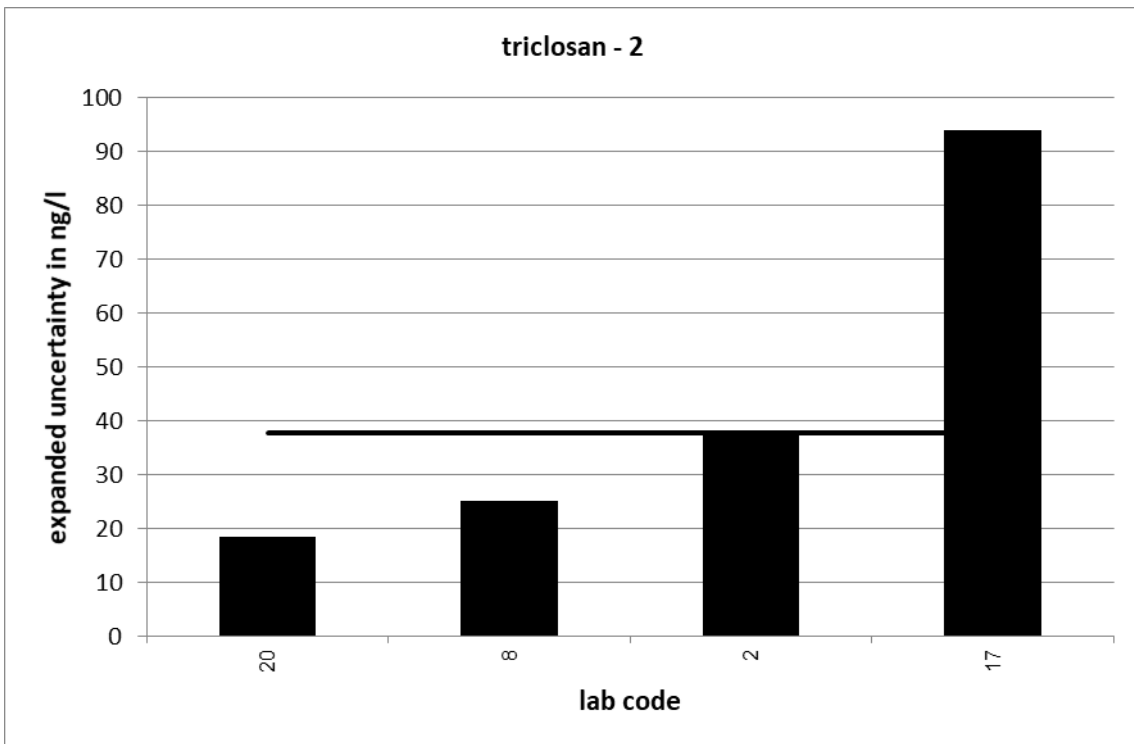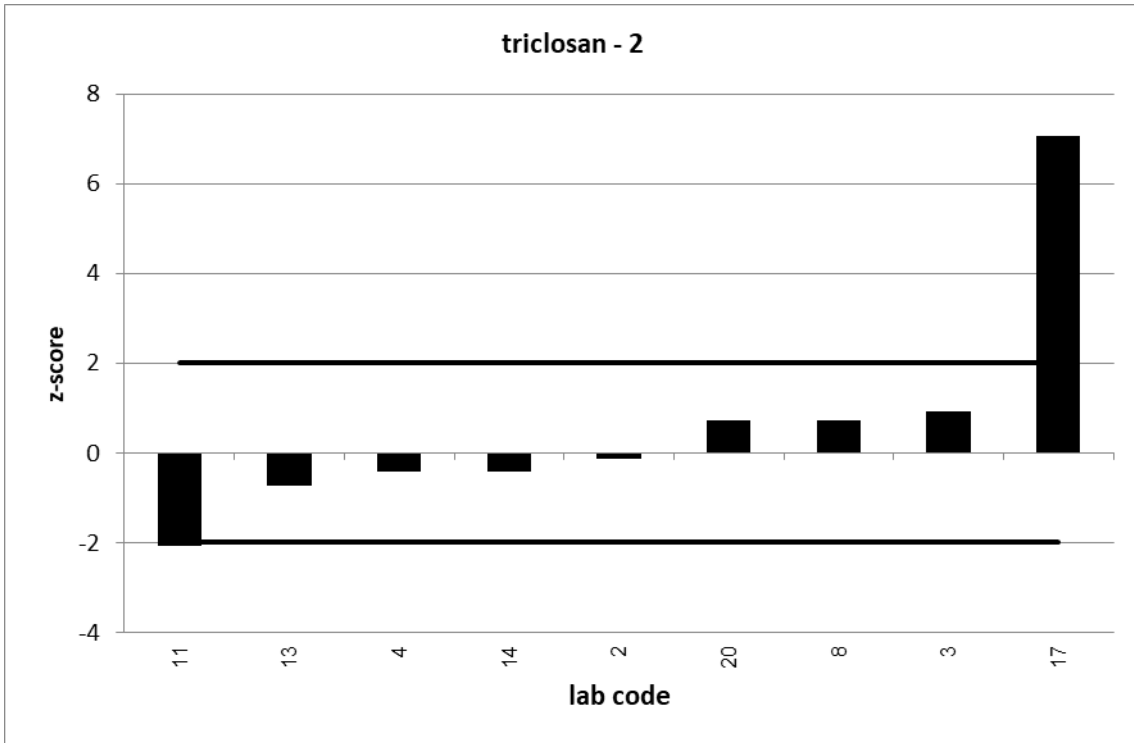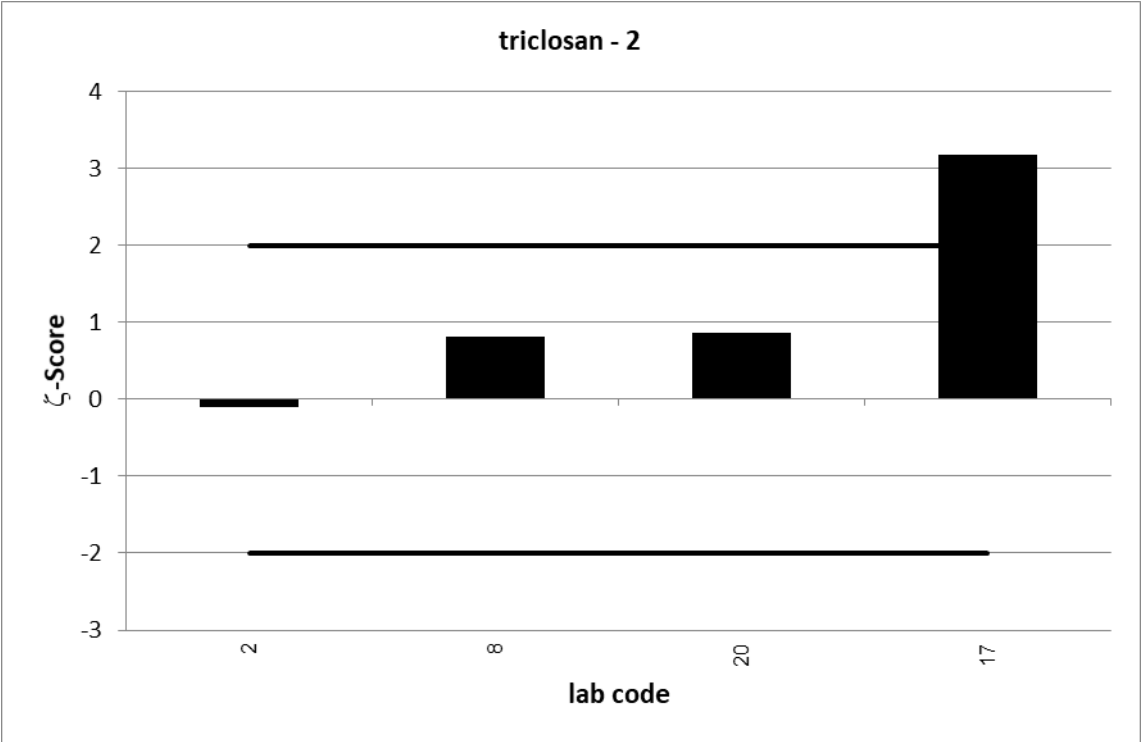
triclosan - 2

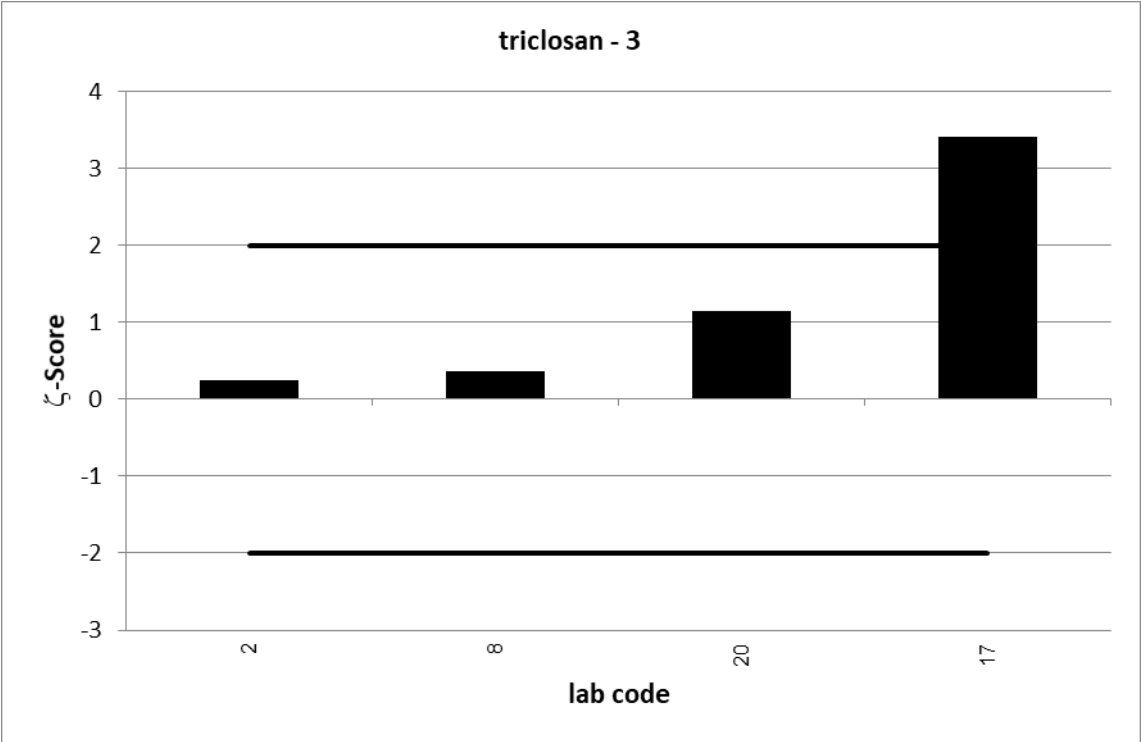| UKWIR PT 13/20	triclosan - 3				
assigned value [ng/l]*		137,7	± 54,5		
upper tolerance limit [ng/l		217,5			
lower tolerance limit [ng/l		75,47			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.**
2	148,9	74,5	0,2	0,3	s
3	191			1,3	s
4	120			-0,6	s
8	150	40,4	0,4	0,3	s
11	63			-2,4	q
13	93,5243			-1,4	s
14	160			0,6	s
17	474	190	3,4	8,4	u
20	175	35	1,2	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%

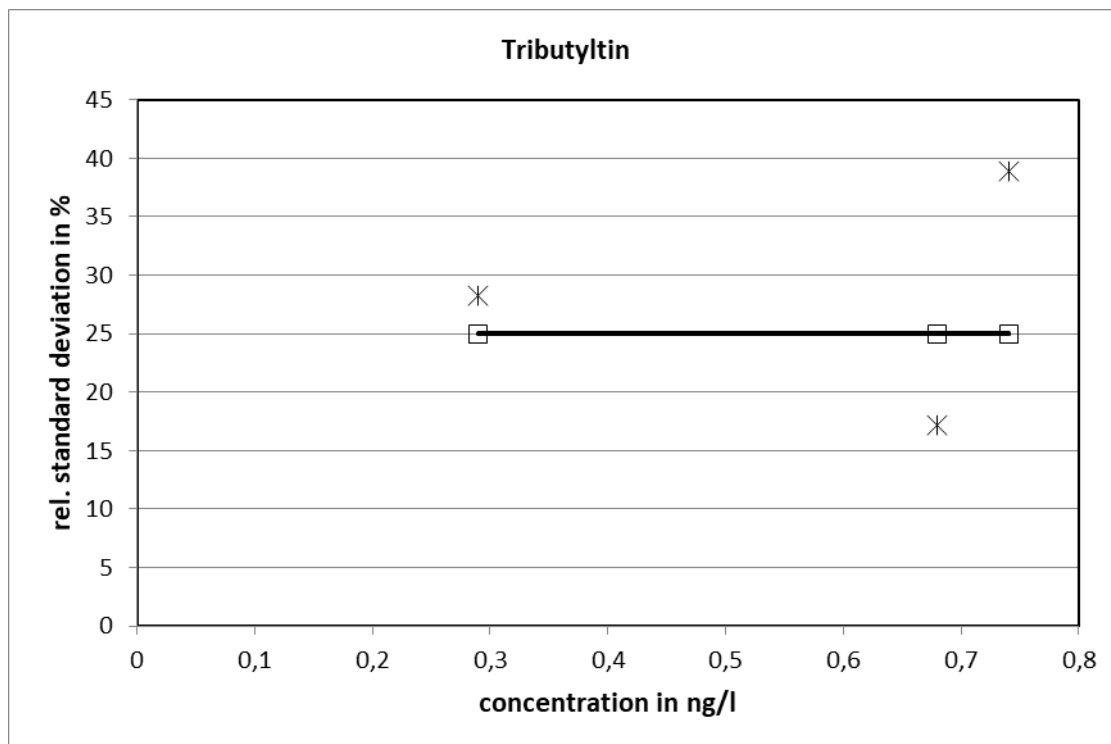** s = satisfactory, q = questionable, u = unsatisfactory

triclosan - 3

triclosan - 3

triclosan - 3

UKWIR 14/20

Tributyltin

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	0,2898	23,55	0,0819	0,0724	25,00	0,4578	0,1588	57,99	-45,19	9	0	3	30,0
2	0,6801	13,56	0,1166	0,1700	25,00	1,074	0,3728	57,99	-45,19	10	0	1	10,0
3	0,7406	30,74	0,2880	0,1852	25,00	1,170	0,4060	57,99	-45,19	10	0	2	20,0
									sum	29	0	6	20,7

Relative standard deviation


25 % is the value used as standard deviation for proficiency assessment.

UKWIR PT 14/20		Tributyltin - 1			
assigned value [ng/l]*		0,2898	± 0,0682		
upper tolerance limit [ng/l		0,4578			
lower tolerance limit [ng/l		0,1588			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.**
1	0,242			-0,7	s
2	0,2779			-0,2	s
3	0,198	0,099	-1,5	-1,4	s
4	4,08	1,07	7,1	45,1	u
5	0,24			-0,8	s
10	0,389	0,078	1,9	1,2	s
11	0,602			3,7	u
14	0,2421			-0,7	s
17	0,27			-0,3	s
18	0,545	0,087	4,6	3,0	u

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Tributyltin - 1

Tributyltin - 1
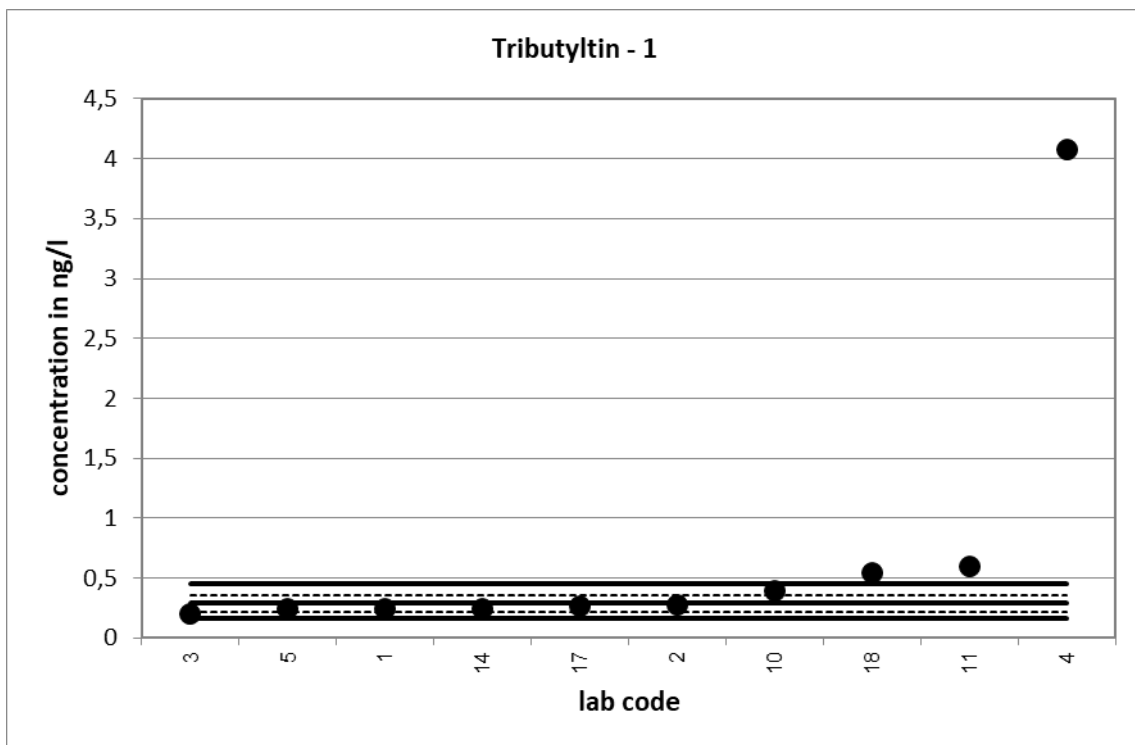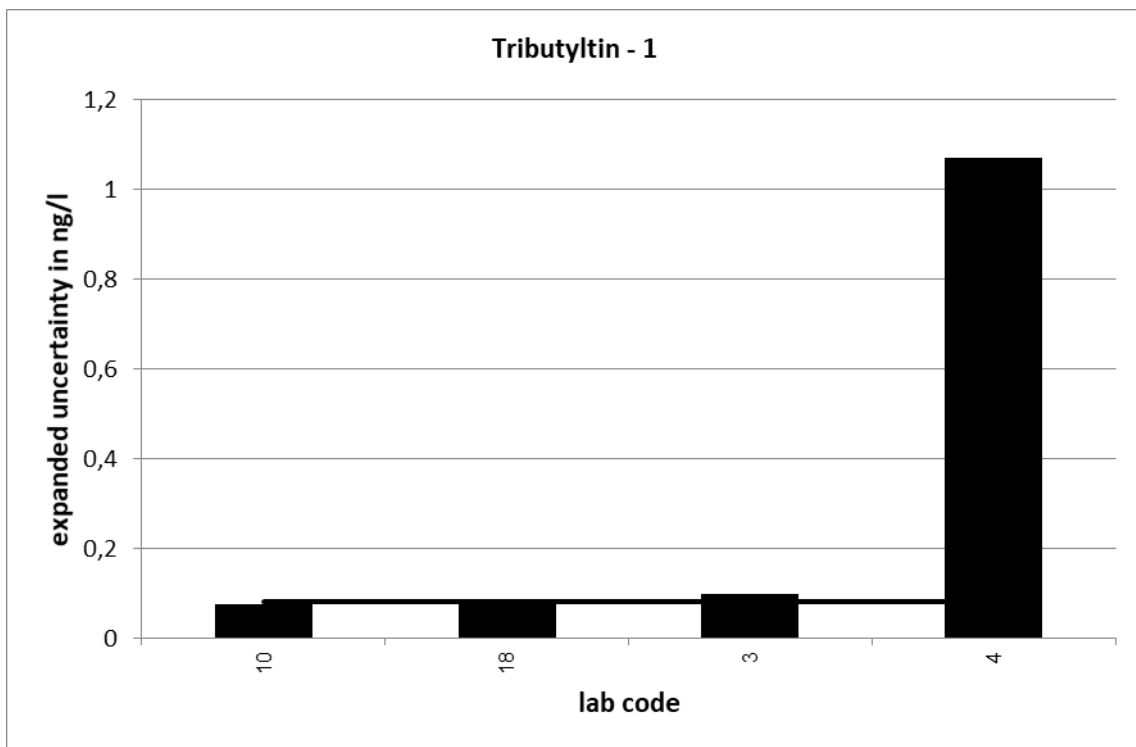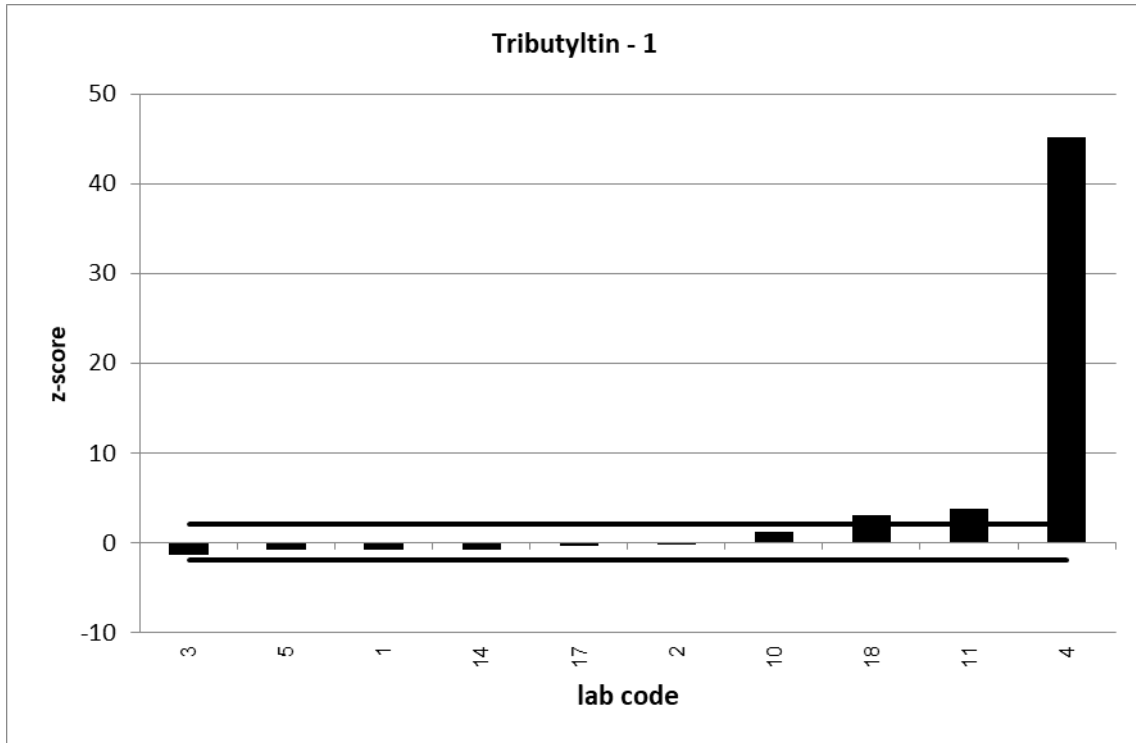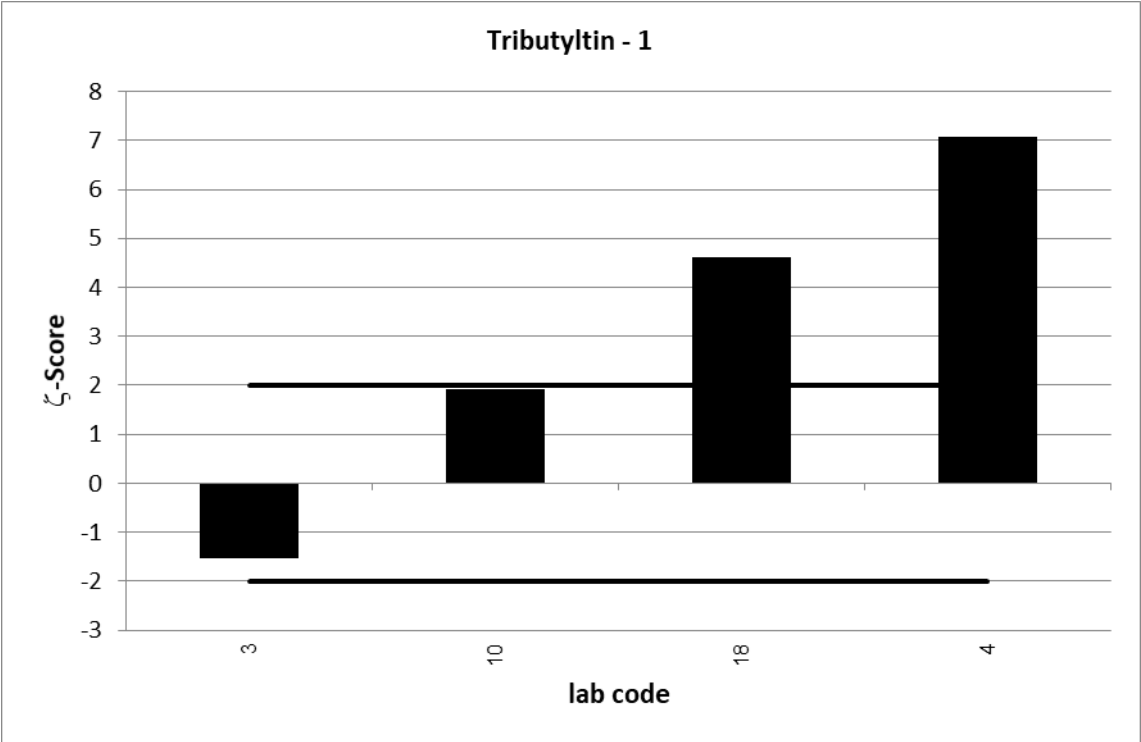
Tributyltin - 1

UKWIR PT 14/20		Tributyltin - 2			
assigned value [ng/l]*		0,6801	± 0,0922		
upper tolerance limit [ng/l		1,074			
lower tolerance limit [ng/l		0,3728			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.**
1	0,679			0,0	s
2	0,6006			-0,5	s
3	0,513	0,256	-1,2	-1,1	s
4	1,15	0,3	3,0	2,4	q
5	0,607			-0,5	s
10	0,66	0,132	-0,2	-0,1	s
11	0,926			1,2	s
14	0,6359			-0,3	s
17	0,66			-0,1	s
18	0,953	0,153	3,1	1,4	s

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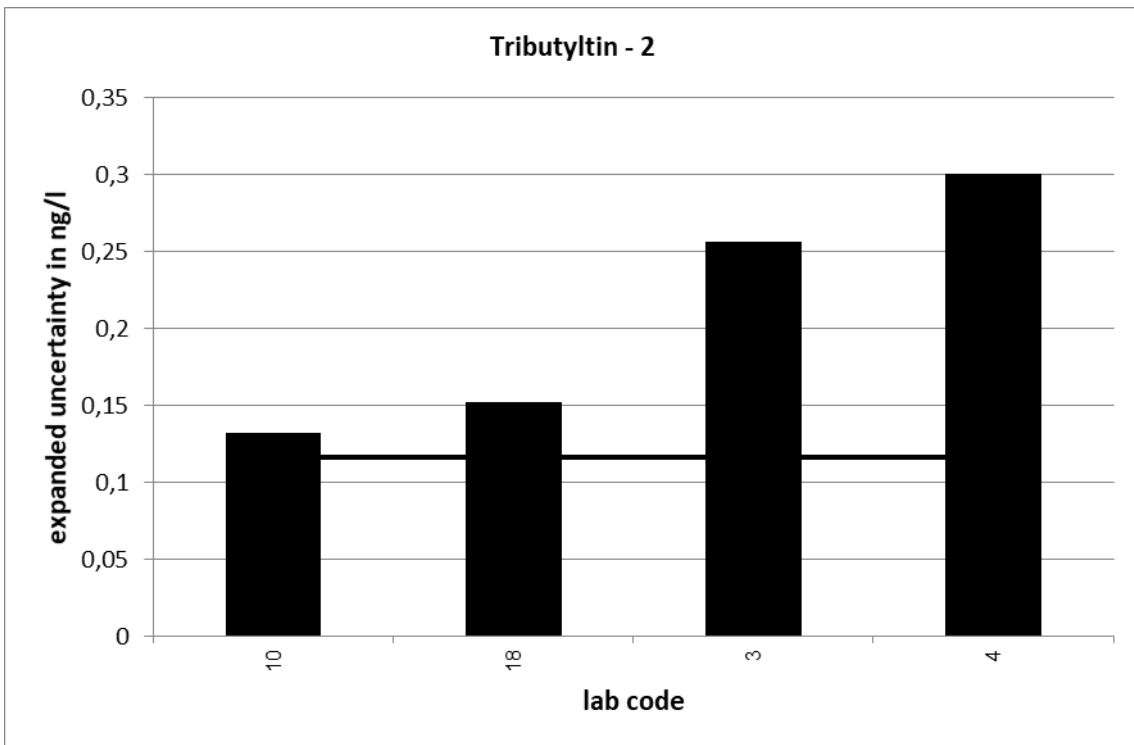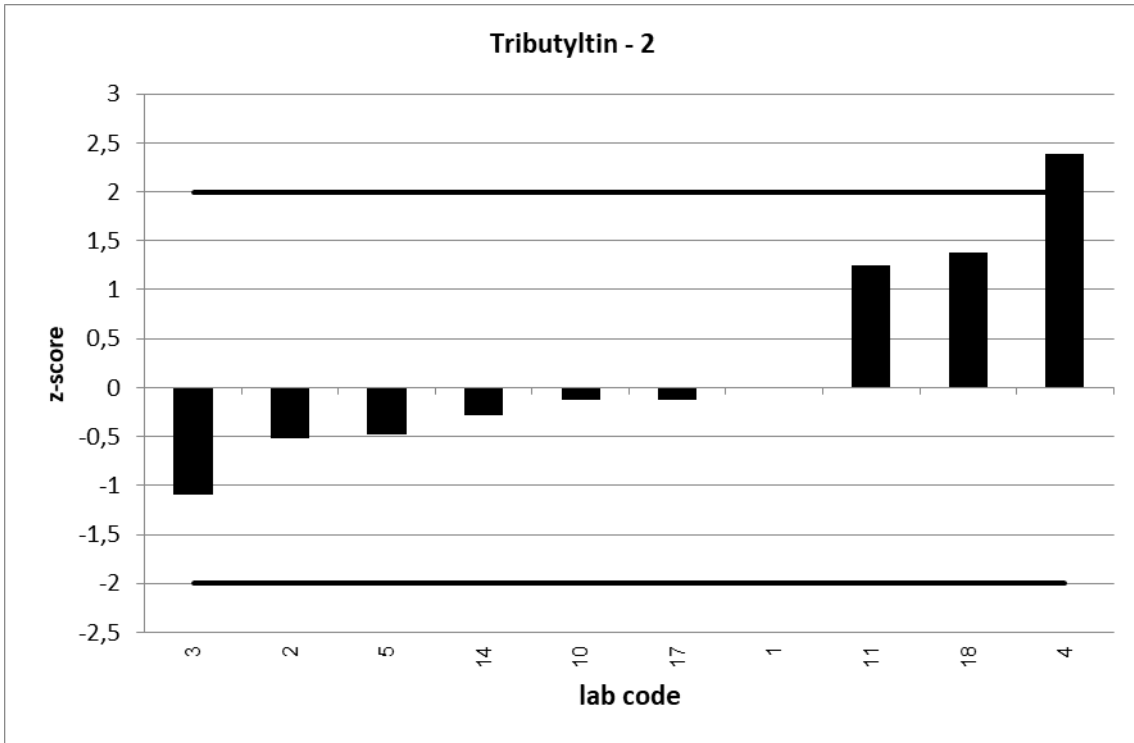** s = satisfactory, q = questionable, u = unsatisfactory
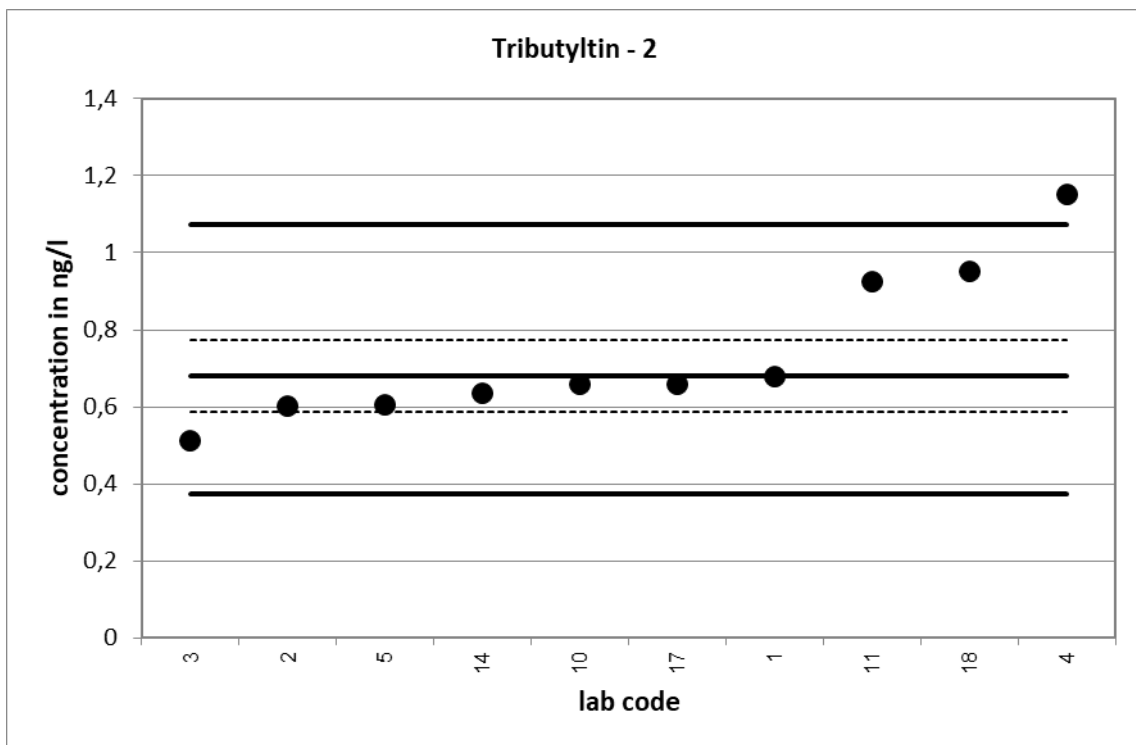
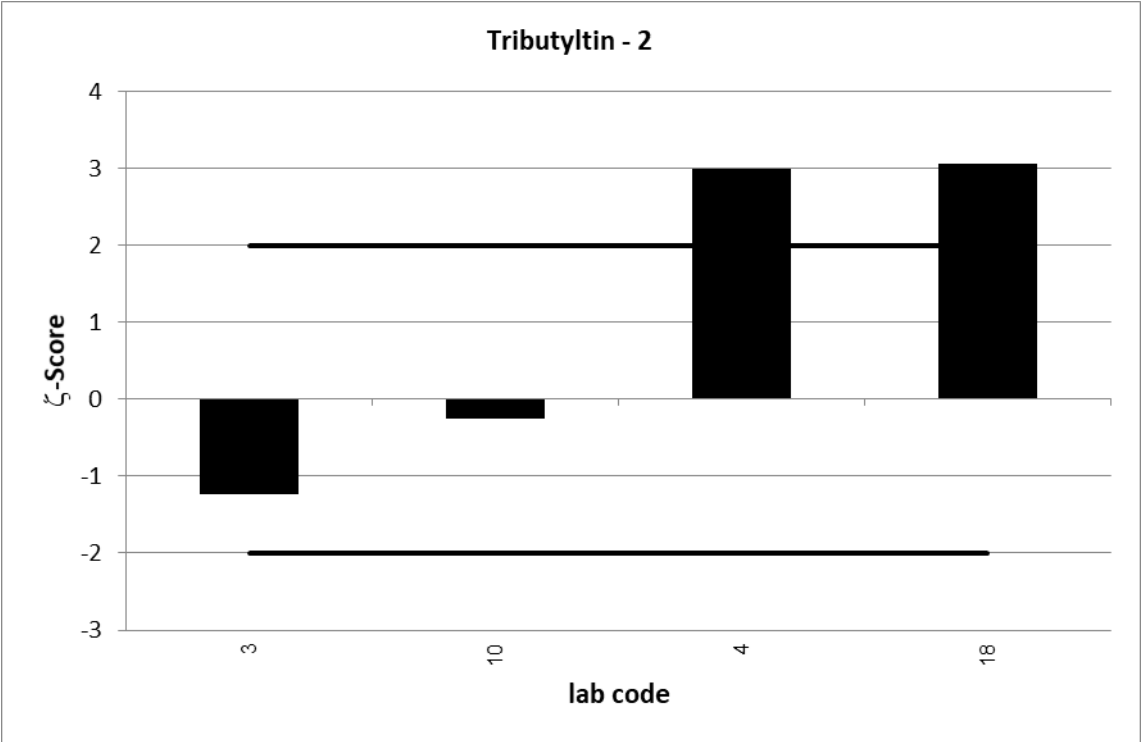

Tributyltin - 2

UKWIR PT 14/20		Tributyltin - 3				
assigned value [ng/l]*			0,7406	± 0,2277		
upper tolerance limit [ng/l			1,17			
lower tolerance limit [ng/l			0,406			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.**	
1	0,723			-0,1	s	
2	0,6721			-0,4	s	
3	0,427	0,213	-2,0	-1,9	s	
4	1,79	0,47	4,0	4,9	u	
5	0,564			-1,1	s	
10	0,877	0,175	0,9	0,6	s	
11	1,51			3,6	u	
14	0,6254			-0,7	s	
17	0,58			-1,0	s	
18	0,778	0,125	0,3	0,2	s	

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Tributyltin - 3