

# Analytische Qualitätssicherung Baden-Württemberg

Proficiency Tests UKWIR 3/18 to 4/18  
priority substances in surface water

hexabromocyclododecane (HBCDD), tributyltin (TBT)

Stuttgart, June 2018

provided by  
AQS Baden-Württemberg  
c/o Institute for Sanitary Engineering, Water Quality and Solid Waste Management,  
University of Stuttgart  
Bandtäle 2, 70569 Stuttgart-Büsnau, Germany

Responsibilities:

Scientific director AQS: Dr.-Ing. Dipl.-Chem. Michael Koch  
PT manager: Dr.-Ing. Frank Baumeister  
Sample preparation: Matthias Mischo

Release of the report: 04 June 2018  
by Scientific director AQS: Dr.-Ing. Michael Koch

AQS Baden-Württemberg at  
Institute of Sanitary Engineering,  
Water Quality and Solid Waste Management  
at University of Stuttgart  
Bandtäle 2  
70569 Stuttgart-Büsnau  
Germany  
<http://www.aqsbw.de>  
Tel.: +49 (0)711 / 685-65446  
Fax: +49 (0)711 / 685-53769  
E-Mail: [info@aqsbw.de](mailto:info@aqsbw.de)

This report is available in the internet on [http://www.aqsbw.de/pdf/report\\_UKWIR\\_3-4\\_18.pdf](http://www.aqsbw.de/pdf/report_UKWIR_3-4_18.pdf).

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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 four rounds the following determinands were to be measured:

- UKWIR 3/18
  - Hexabromocyclododecane (HBCDD)
- UKWIR 4/18
  - Tributyltin

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

## PT design

Each participant received the following samples:

- 3 spiked samples for the determination of the respective determinands based on a filtered surface water sample in 1000-ml-ground bottles with ground-in stopper
- 1 blank sample of the filtered surface water

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 (TNT). 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
HBCDD	0.0092 µg/l
TBT	0.12 ng/l

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 µg/l for HBCDD and in ng/l for TBT 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 assigned value  $x_{pt}$  was derived from the Hampel estimator for HBCDD and TBT. The uncertainty of the assigned values was calculated according to ISO 13528 from the standard deviation derived from the Q method:

$$u(x_{pt}) = 1.25 * \frac{s *}{\sqrt{p}}$$

The standard deviation for proficiency assessment  $\sigma_{pt}$  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  $\sigma_{pt}$ :

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

The assessment of the results was as follows:

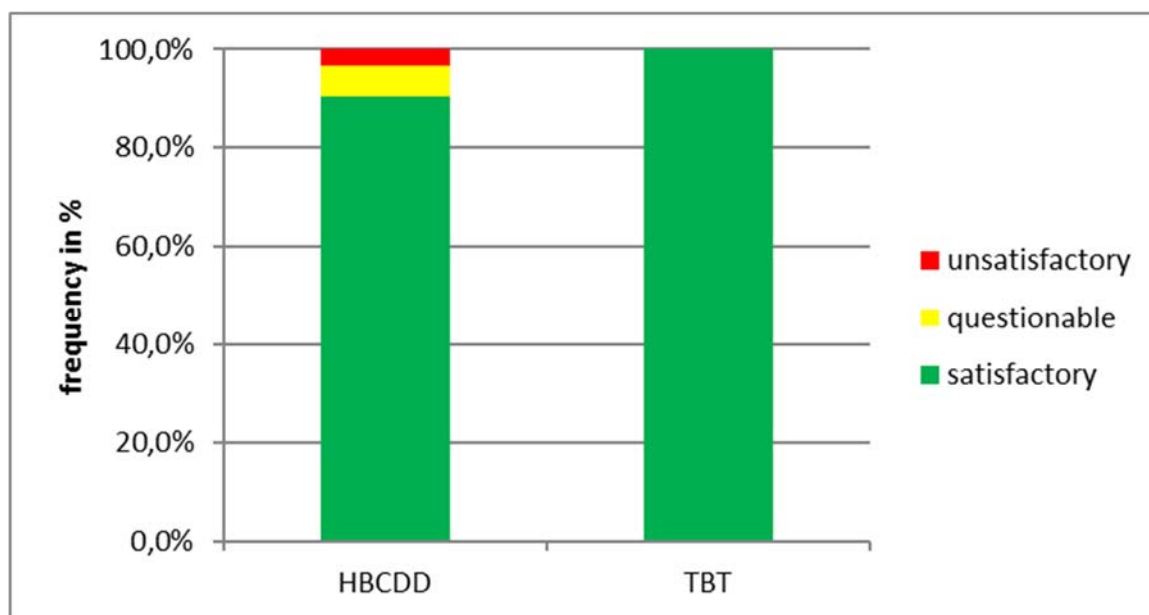
$ z  \leq 2.0$	satisfactory
$2.0 <  z  < 3.0$	questionable
$ z  \geq 3.0$	unsatisfactory

## Results of evaluation

### Number of participants:

PT round	Determinands	Number of participants	Number of participants reporting results
UKWIR 3/18	HBCDD	11	11
UKWIR 4/18	TBT	11	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  $\mu\text{g/l}$
- expanded uncertainty of the assigned value in %
- standard deviation of the data set in  $\mu\text{g/l}$ , 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  $\mu\text{g/l}$  for the calculation of z-scores (25 % of the assigned value)
- rel. standard deviation for proficiency assessment in %
- tolerance limits above and below in  $\mu\text{g/l}$  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.

### Used methods

The percentage of analytical techniques used are shown here.

### Sample table

In this table all results of the participants are noted together with uncertainties (where reported). For these uncertainties  $\zeta$ -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

$\zeta$ -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  $\leq 2,0$  can be regarded as 'satisfactory'.

$\zeta$ -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 ( $z = \pm 2,0$ ).

### 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.

### $\zeta$ -score graphs

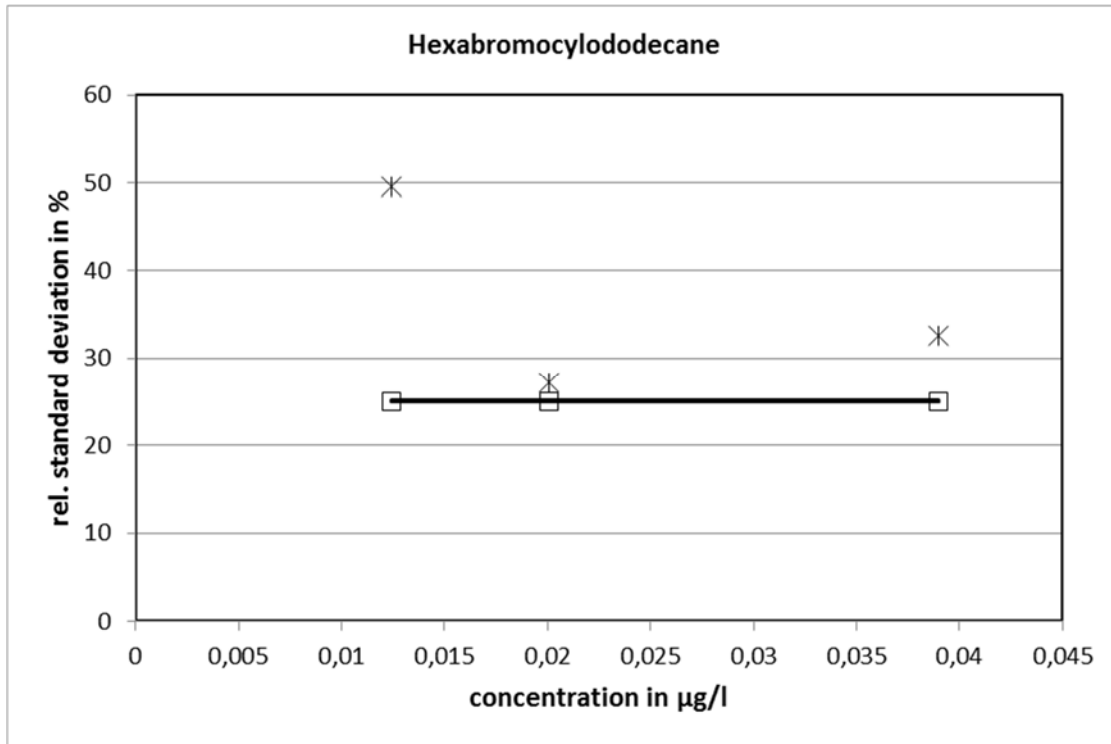
If laboratories reported uncertainties,  $\zeta$ -scores were calculated and are shown versus the laboratory codes.

**UKWIR 3/18**

<b>Hexabromocyclododecane</b>													
level	assigned value [µg/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [µg/l]	standard deviation for proficiency assessment [µg/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [µg/l]	lower tolerance limit [µg/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,0201	20,48	0,0055	0,0050	25,00	0,0301	0,0100	50,00	-50,00	11	0	1	9,1
2	0,0124	41,30	0,0062	0,0031	25,00	0,0186	0,0062	50,00	-50,00	9	1	1	22,2
3	0,0390	24,53	0,0127	0,0097	25,00	0,0585	0,0195	50,00	-50,00	11	0	0	0,0
									sum	31	1	2	9,7

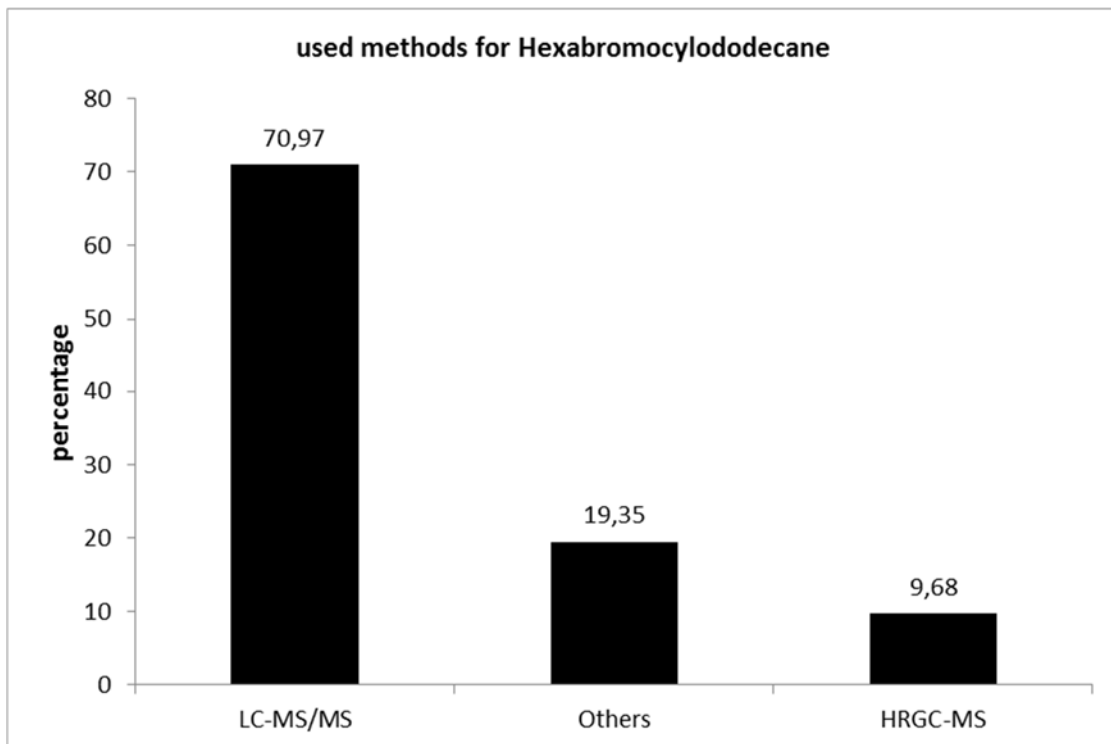


**Relative standard deviation**



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

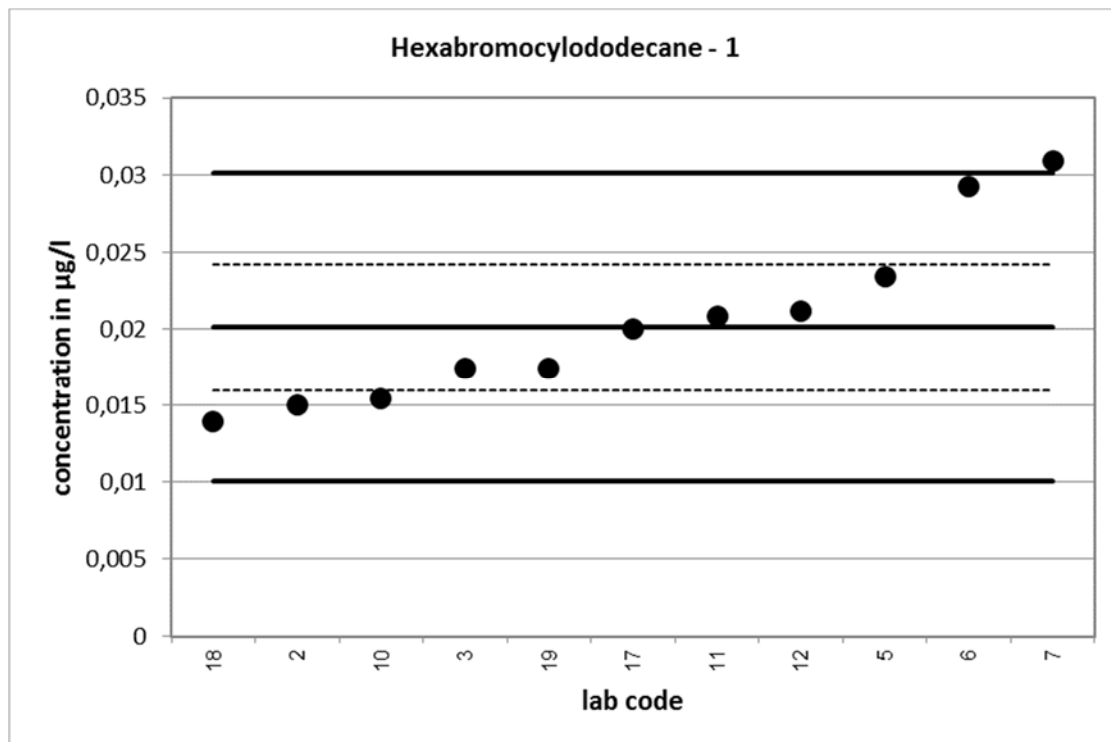
**Used methods**

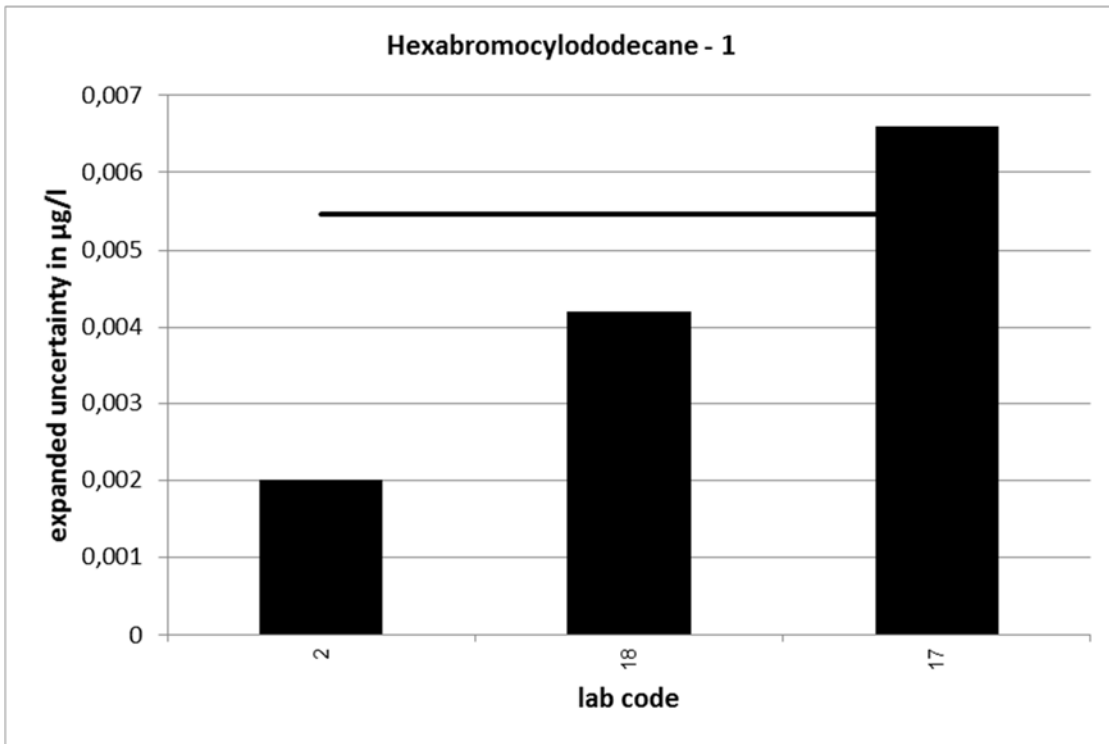
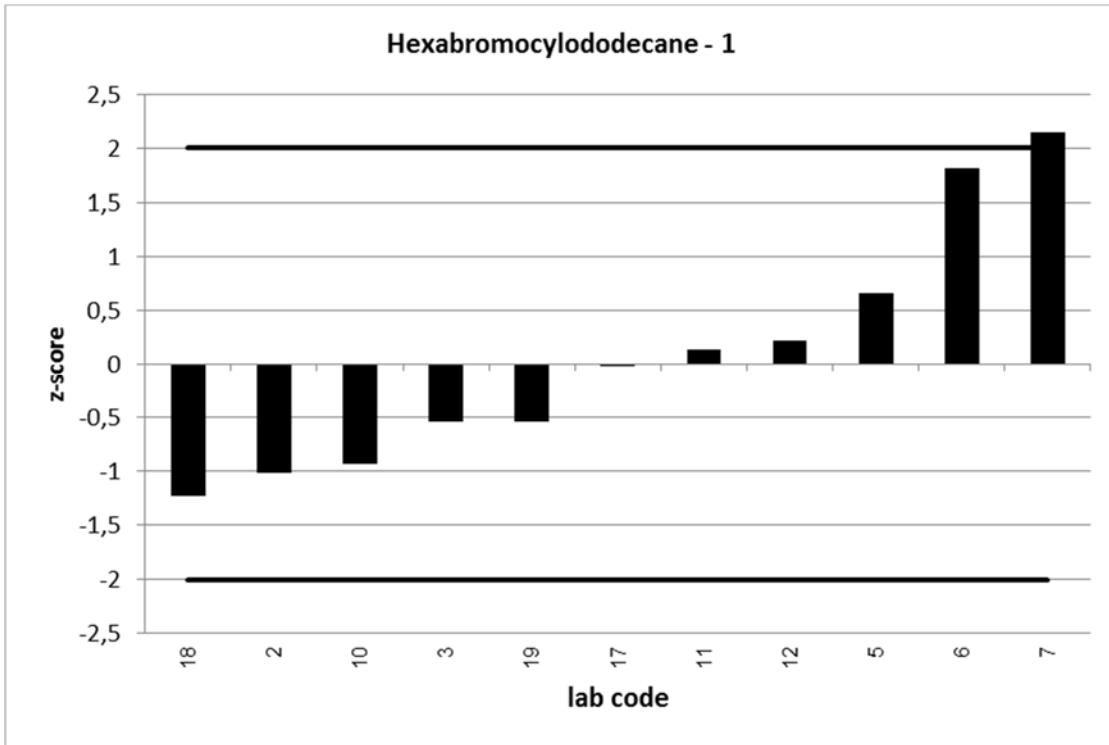


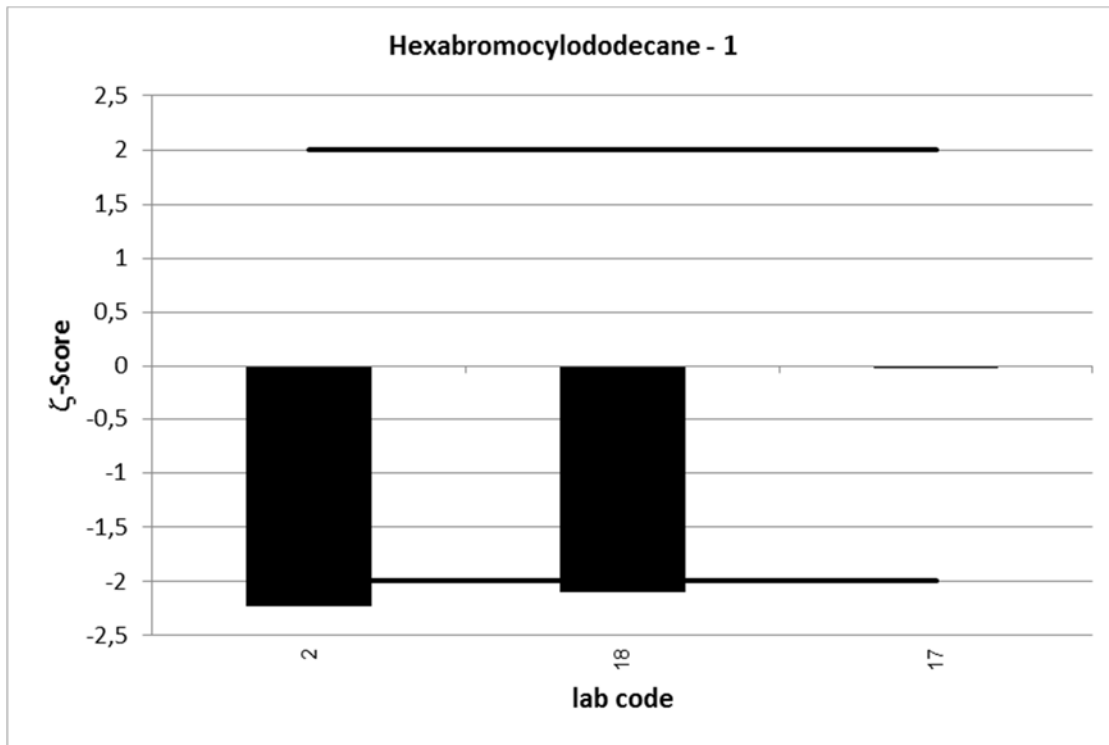
UKWIR 3/18		Hexabromocyclododecane - 1			
assigned value [ $\mu\text{g/l}$ ]*		0,0201 $\pm$ 0,00412			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,03015			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,01005			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	$\zeta$ -score	z-score	assessm.**
2	0,015	0,002	-2,2	-1,0	s
3	0,0174			-0,5	s
5	0,0234			0,7	s
6	0,0292			1,8	s
7	0,0309			2,1	q
10	0,0154			-0,9	s
11	0,0208			0,1	s
12	0,0212			0,2	s
17	0,02	0,007	0,0	0,0	s
18	0,0139	0,004	-2,1	-1,2	s
19	0,0174			-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



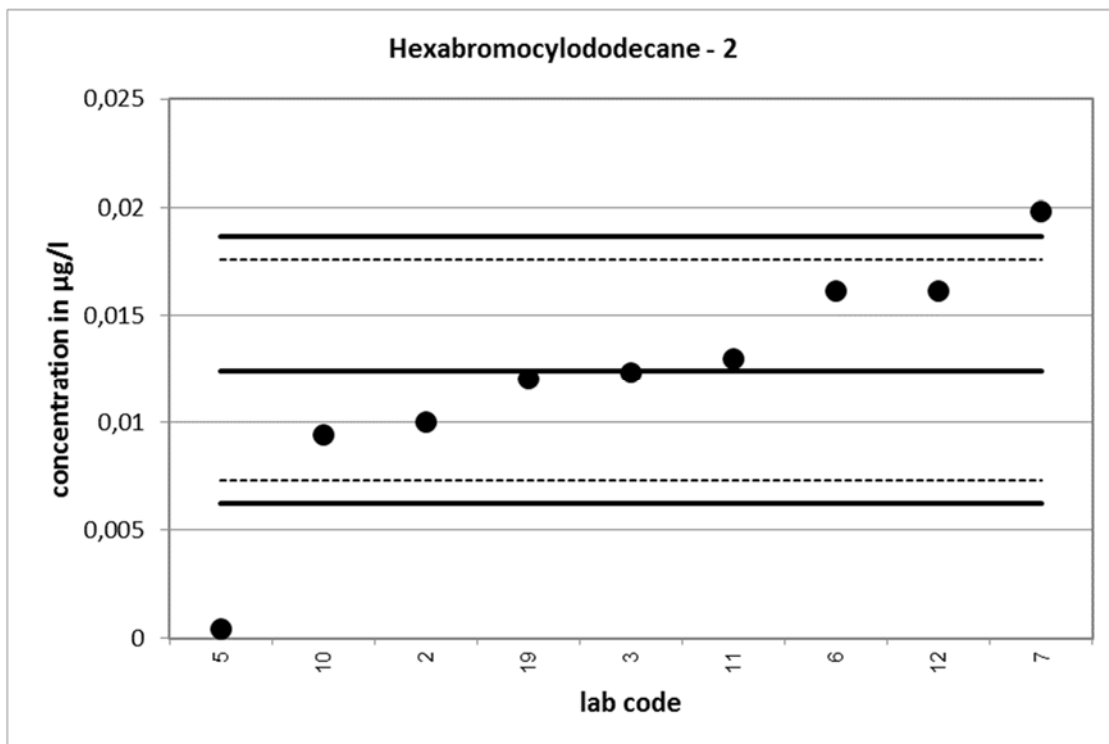


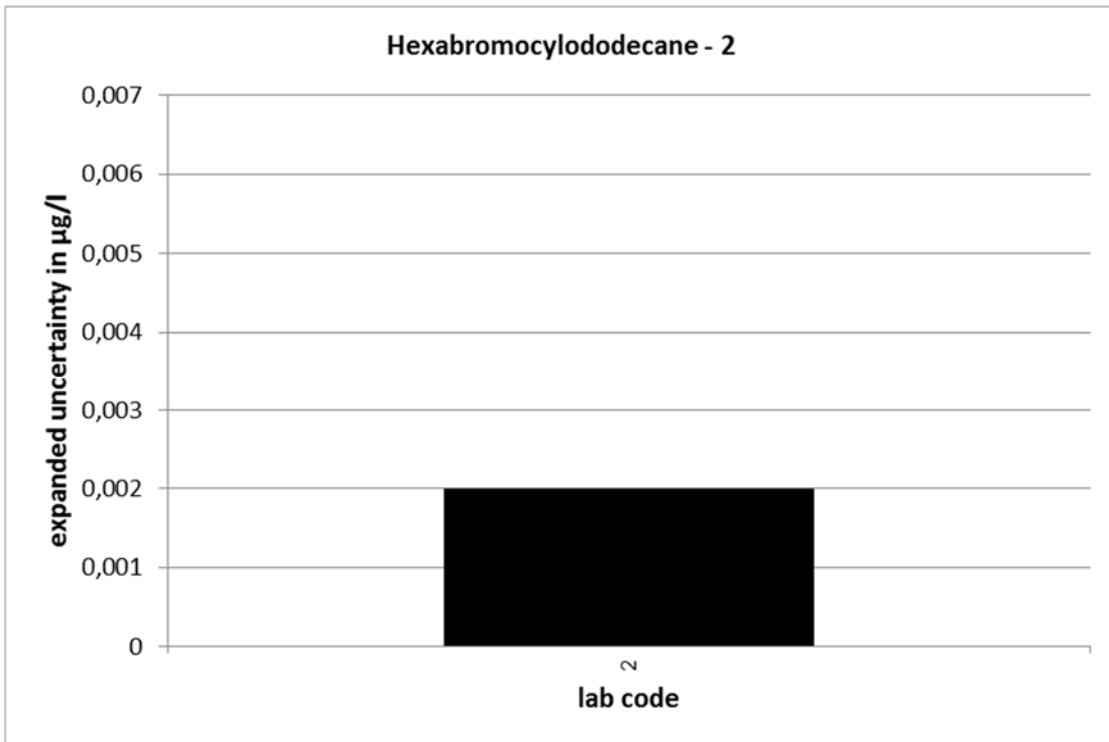
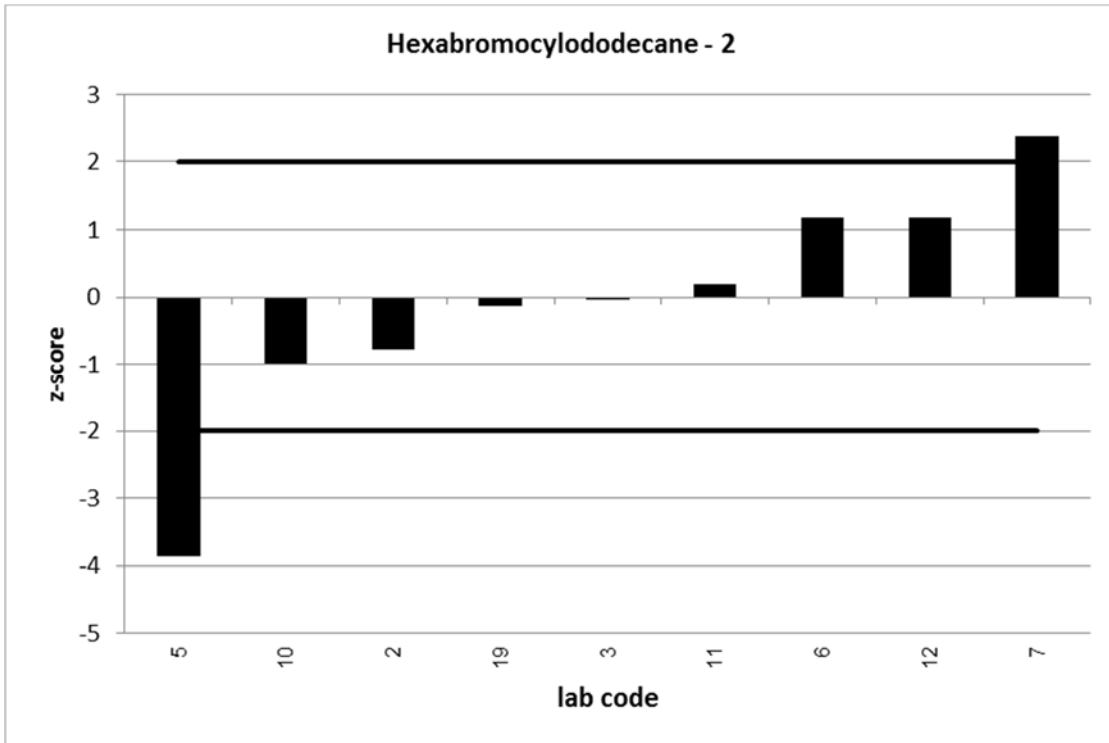


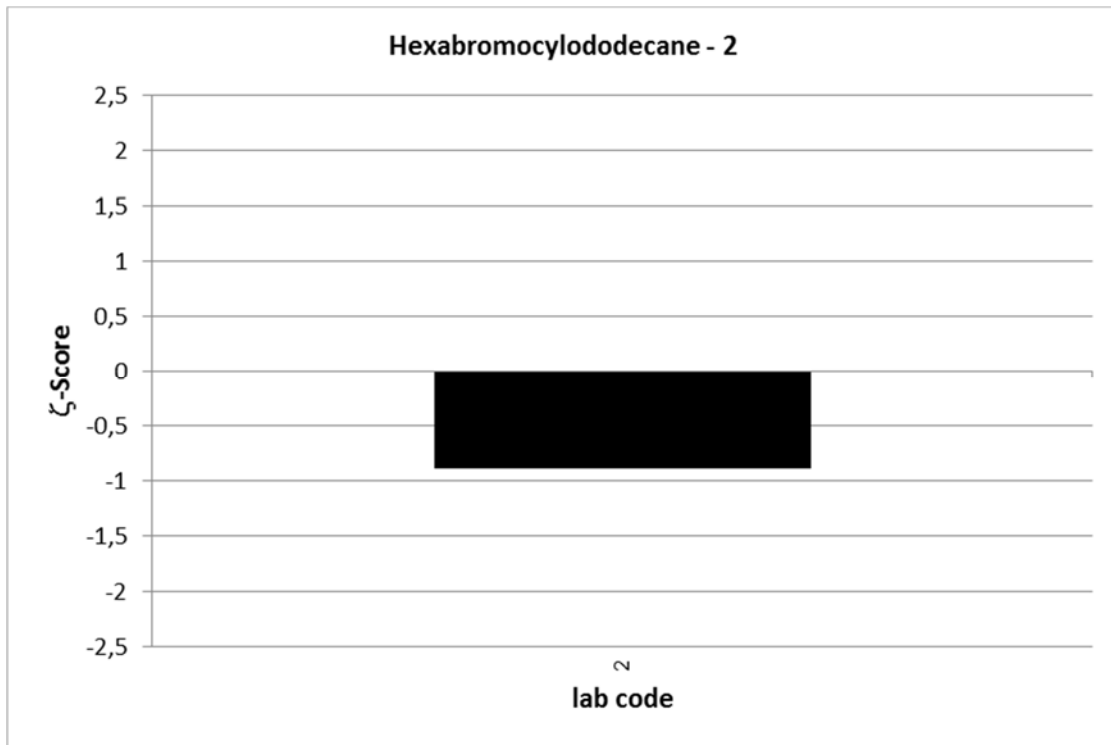
UKWIR 3/18		Hexabromocyclododecane - 2			
assigned value [ $\mu\text{g/l}$ ]*		0,01243 $\pm$ 0,00513			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,01865			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,006215			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	$\zeta$ -score	z-score	assessm.**
2	0,01	0,002	-0,9	-0,8	s
3	0,0123			0,0	s
5	0,000418			-3,9	u
6	0,0161			1,2	s
7	0,0198			2,4	q
10	0,00938			-1,0	s
11	0,013			0,2	s
12	0,0161			1,2	s
19	0,012			-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



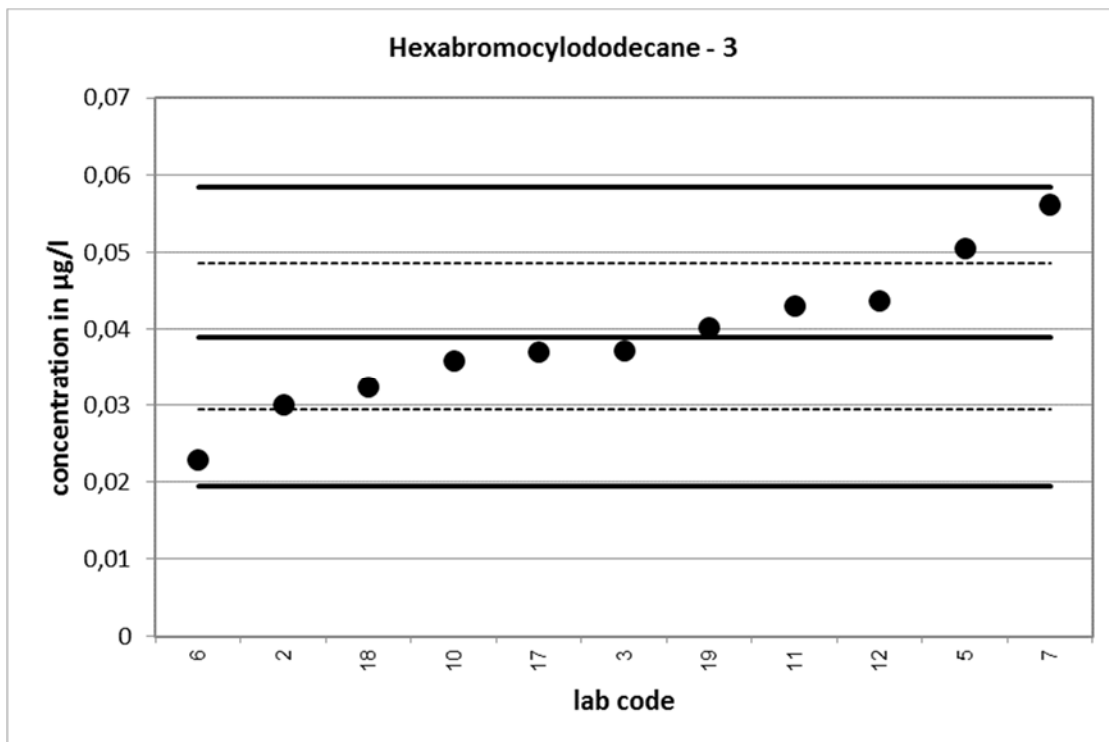




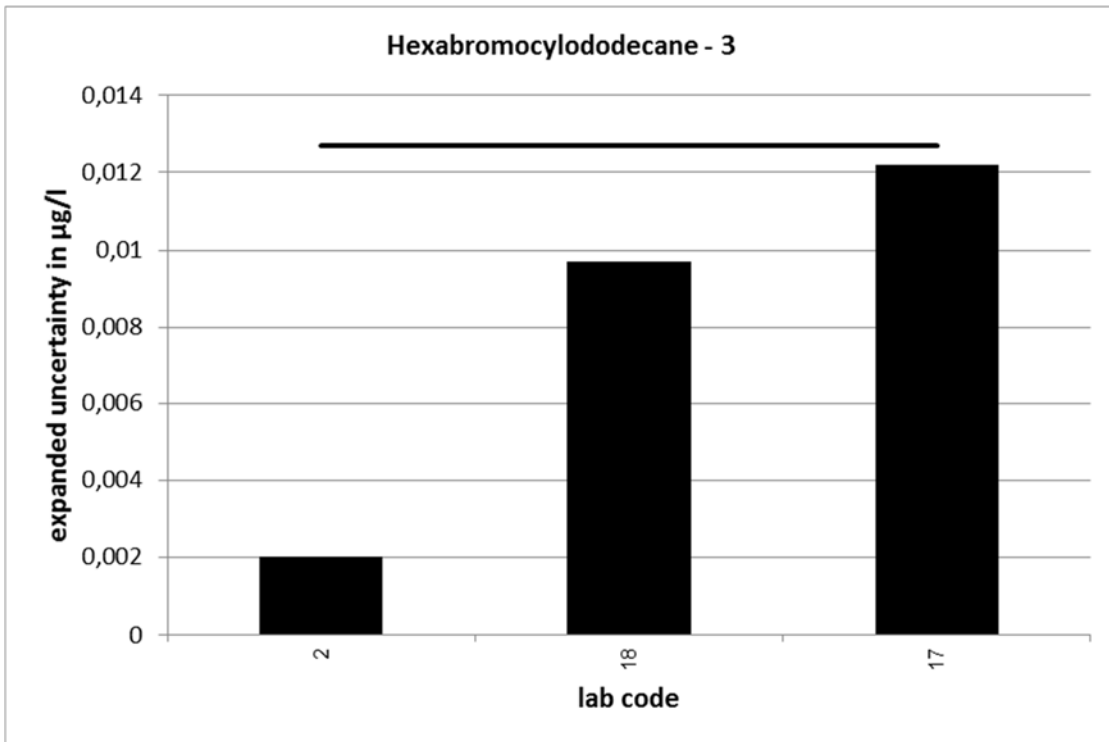
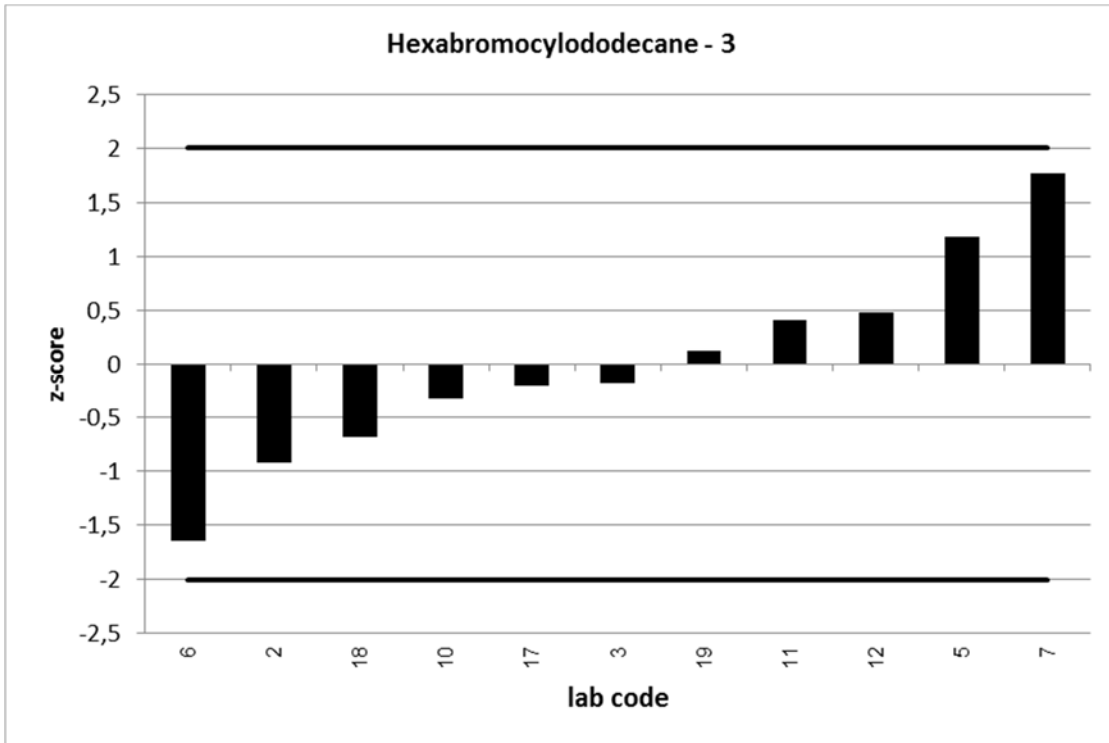
UKWIR 3/18		Hexabromocyclododecane - 3			
assigned value [ $\mu\text{g/l}$ ]*		0,03898 $\pm$ 0,00956			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,05847			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,01949			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	$\zeta$ -score	z-score	assessm.**
2	0,03	0,002	-1,8	-0,9	s
3	0,0372			-0,2	s
5	0,0505			1,2	s
6	0,0229			-1,7	s
7	0,0562			1,8	s
10	0,0358			-0,3	s
11	0,043			0,4	s
12	0,0437			0,5	s
17	0,037	0,012	-0,3	-0,2	s
18	0,0323	0,01	-1,0	-0,7	s
19	0,0402			0,1	s

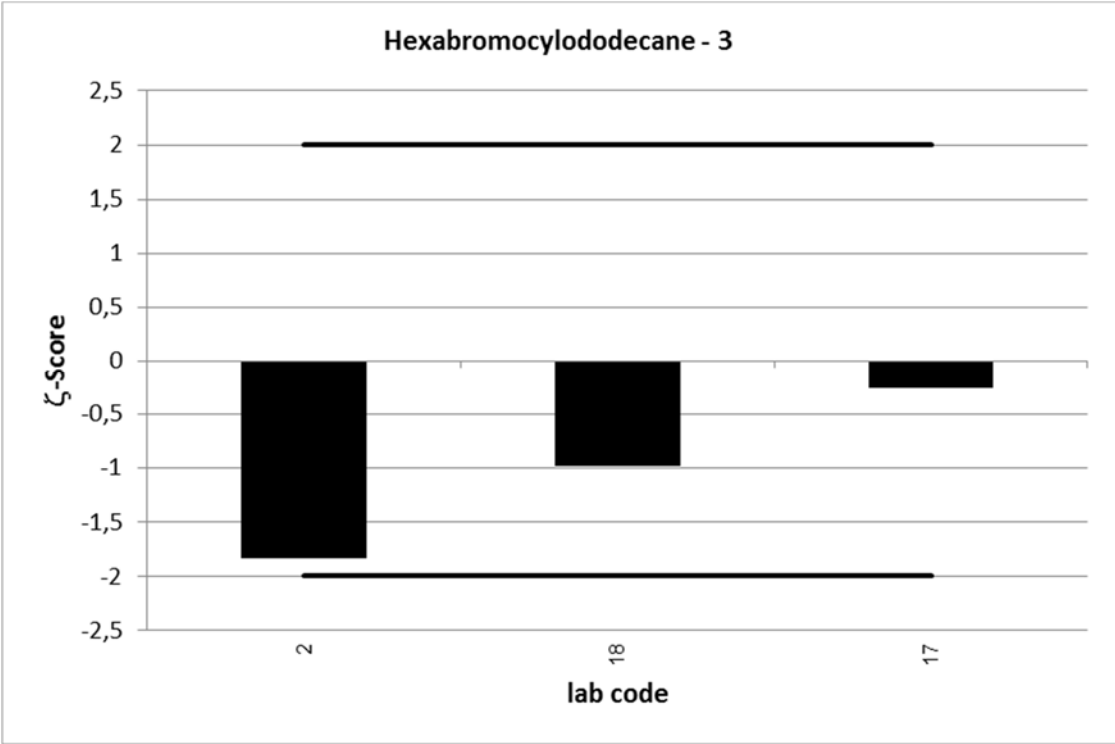
\* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor  $k=2$  corresponding to a confidence level of about 95%

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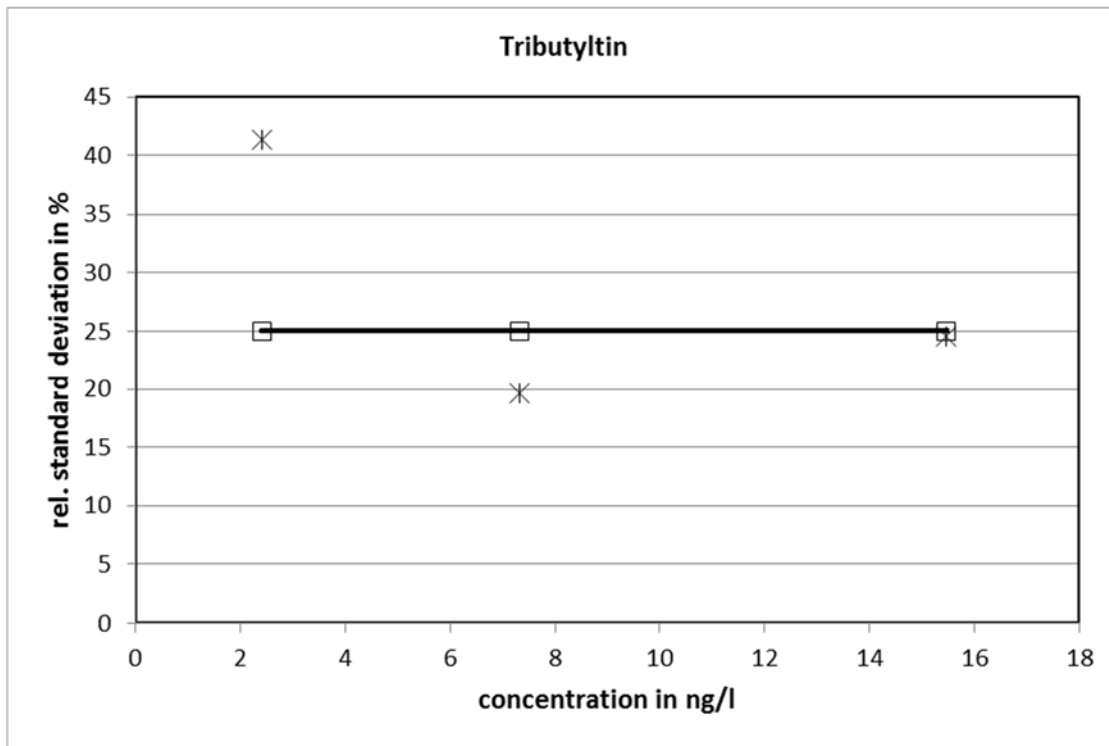




# Tributyltin

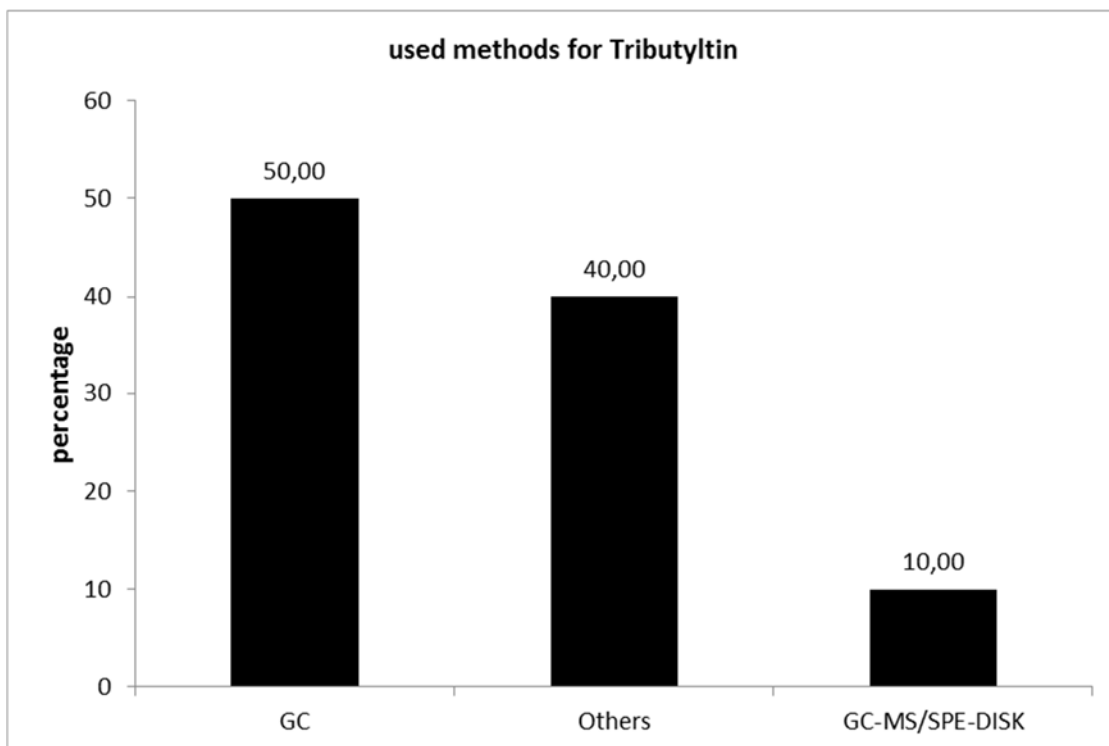
level	assigned value [ng/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [ng/l]	standard deviation for proficiency assessment [ng/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [ng/l]	lower tolerance limit [ng/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	2,408	32,71	0,9962	0,6019	25,00	3,611	1,204	50,00	-50,00	10	0	0	0,0
2	15,46	19,44	3,800	3,864	25,00	23,18	7,728	50,00	-50,00	10	1	0	10,0
3	7,322	15,51	1,437	1,831	25,00	10,98	3,661	50,00	-50,00	10	0	0	0,0
									sum	30	1	0	3,3

**Relative standard deviation**



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

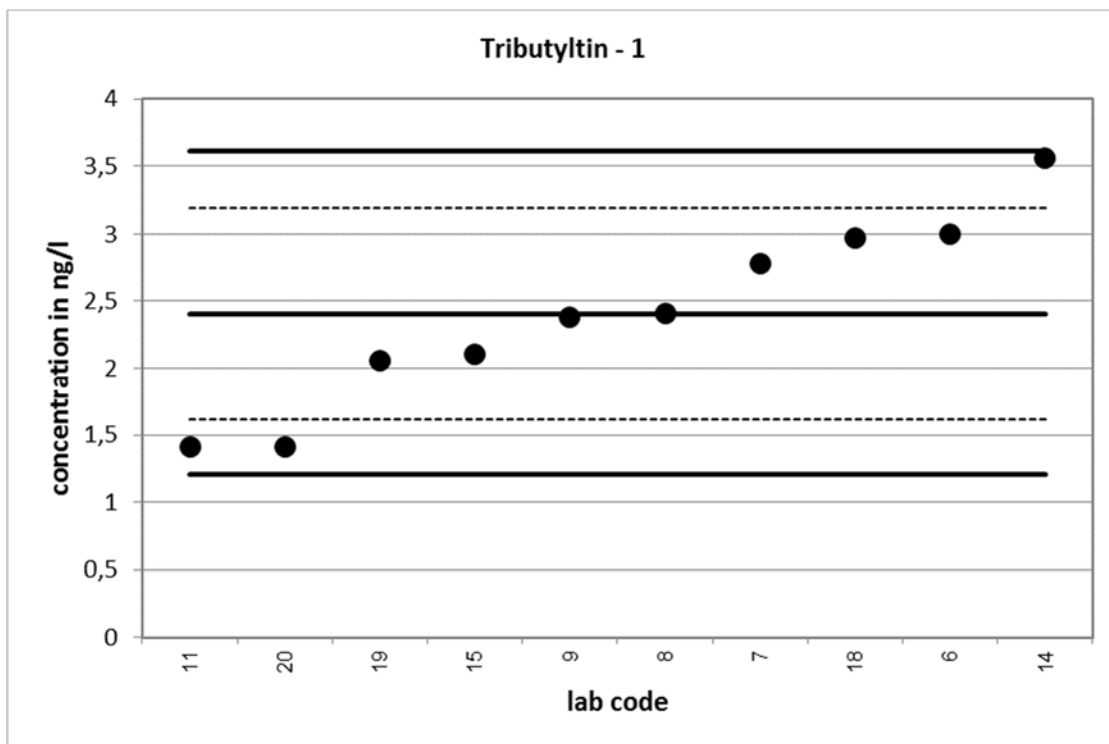
**Used methods**

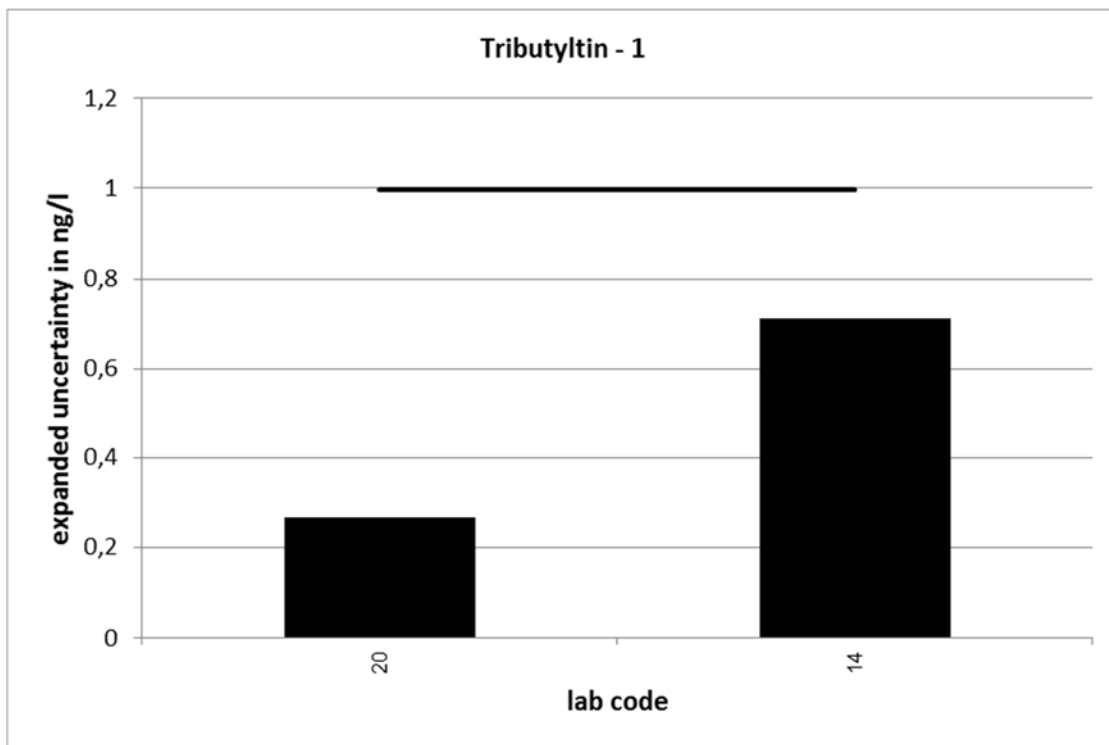


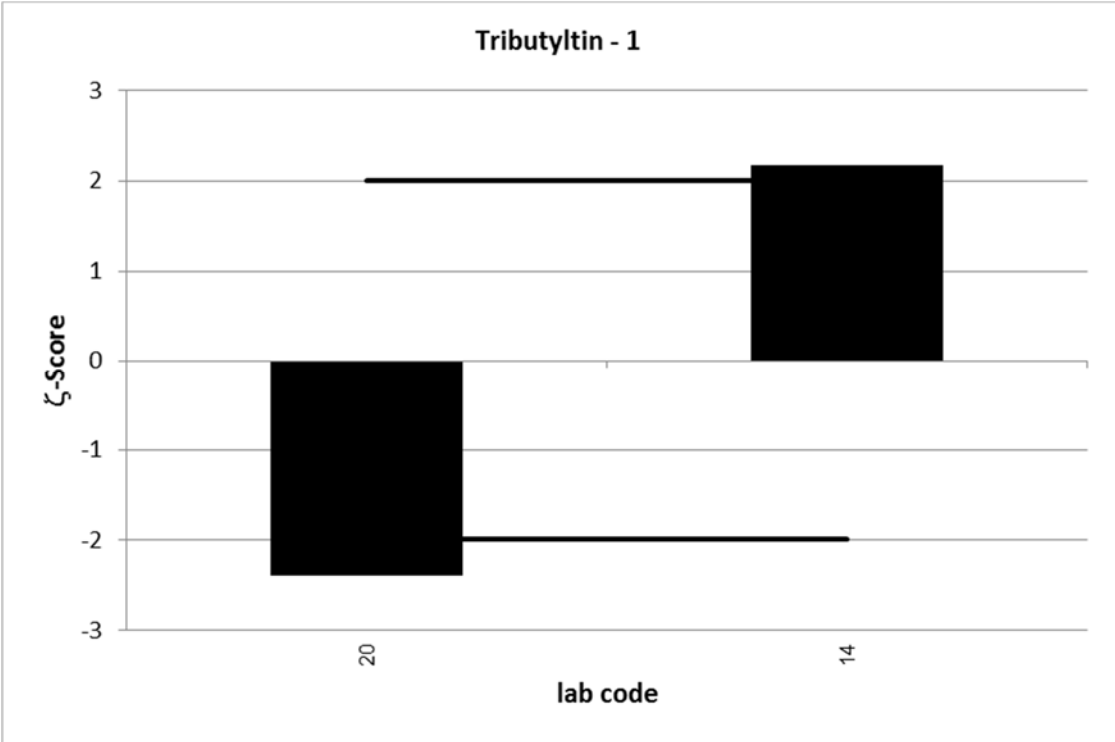
UKWIR 4/18		Tributyltin - 1			
assigned value [ng/l]*		2,408 ± 0,788			
upper tolerance limit [ng/l]		3,611			
lower tolerance limit [ng/l]		1,204			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.**
6	3			1,0	s
7	2,78			0,6	s
8	2,405			0,0	s
9	2,38			0,0	s
11	1,41			-1,7	s
14	3,56	0,713	2,2	1,9	s
15	2,101			-0,5	s
18	2,97			0,9	s
19	2,06			-0,6	s
20	1,41	0,267	-2,4	-1,7	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



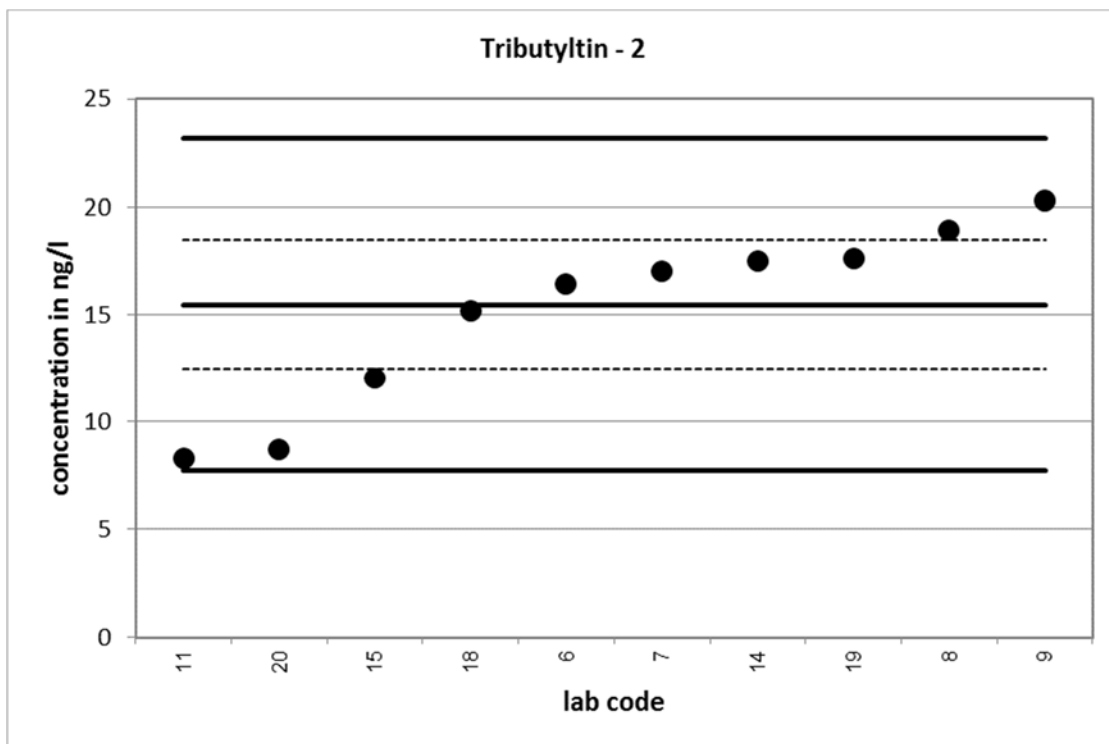




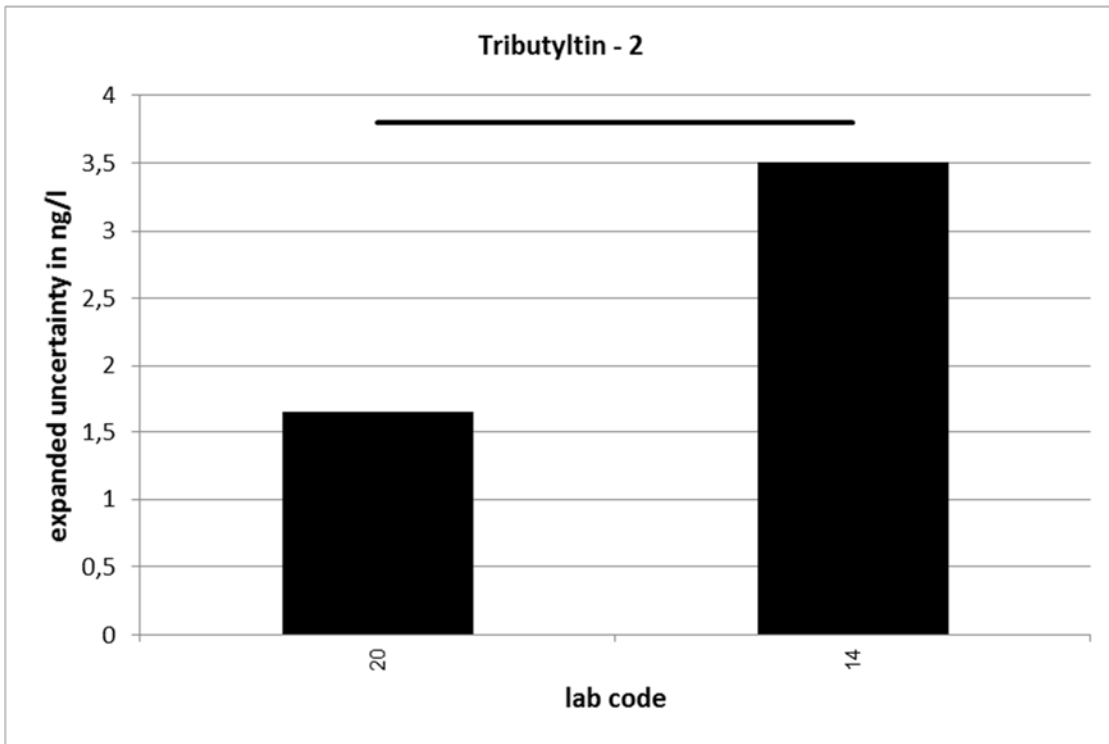
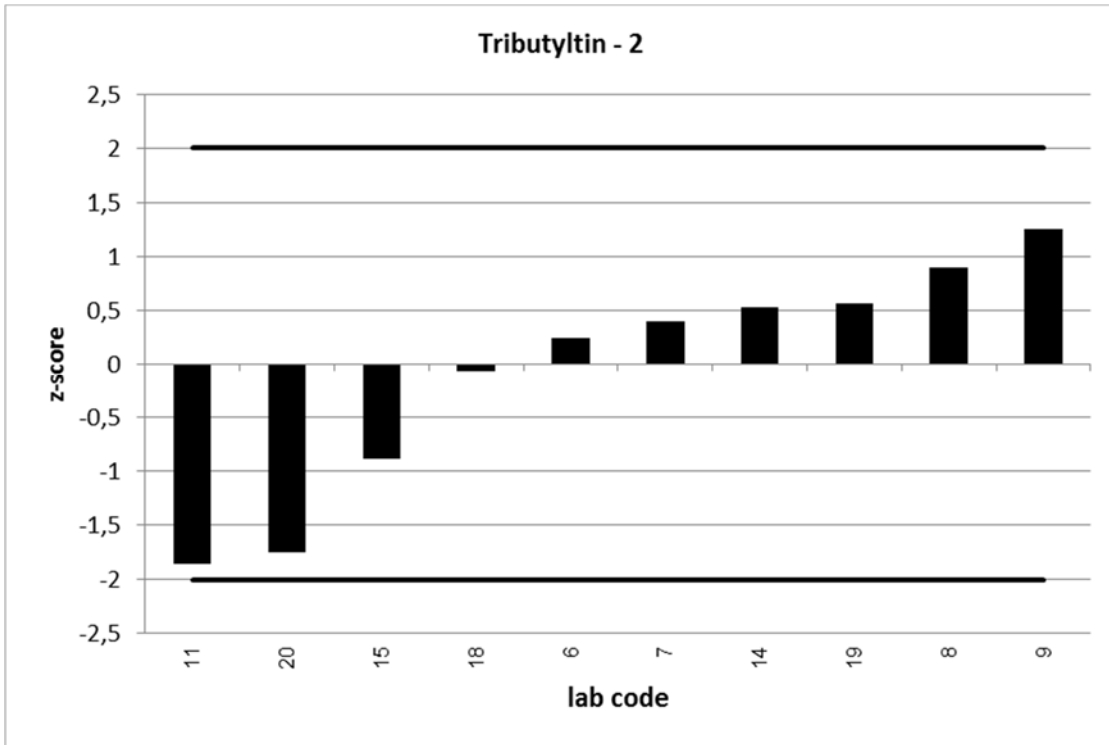
UKWIR 4/18		Tributyltin - 2			
assigned value [ng/l]*		15,46 ± 3			
upper tolerance limit [ng/l]		23,18			
lower tolerance limit [ng/l]		7,728			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.**
6	16,4			0,2	s
7	17			0,4	s
8	18,949			0,9	s
9	20,3			1,3	s
11	8,25			-1,9	s
14	17,5	3,5	0,9	0,5	s
15	12,053			-0,9	s
18	15,2			-0,1	s
19	17,64			0,6	s
20	8,7	1,65	-3,9	-1,7	s

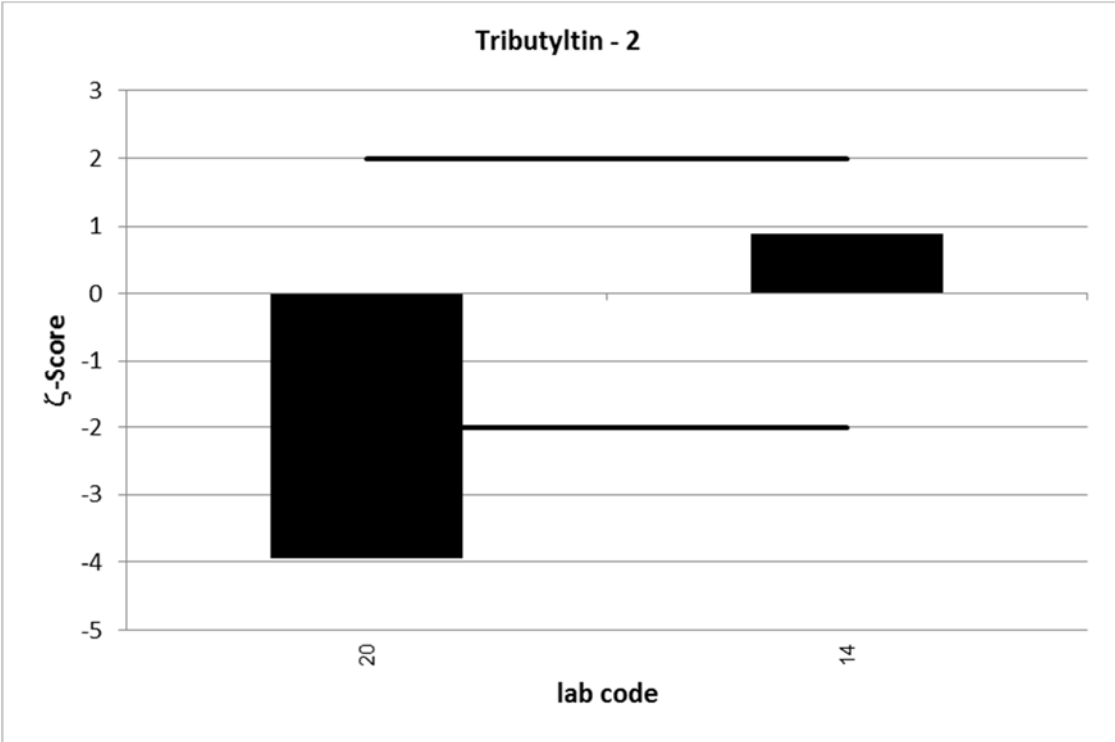
\* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

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UKWIR 4/18		Tributyltin - 3			
assigned value [ng/l]*		7,322 ± 1,136			
upper tolerance limit [ng/l]		10,98			
lower tolerance limit [ng/l]		3,661			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.**
6	8,2			0,5	s
7	8,54			0,7	s
8	7,027			-0,2	s
9	8,83			0,8	s
11	4,38			-1,6	s
14	8,57	1,71	1,2	0,7	s
15	6,111			-0,7	s
18	7,92			0,3	s
19	7,69			0,2	s
20	5,02	0,954	-3,1	-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

