

# Analytische Qualitätssicherung Baden-Württemberg

Proficiency Tests UKWIR 9/17 and 10/17  
priority substances in surface water

Final report

cypermethrin, hexabromocyclododecane

Stuttgart, March 2018

provided by  
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This report is available in the internet on [http://www.aqsbw.de/pdf/report\\_UKWIR\\_9-10\\_17.pdf](http://www.aqsbw.de/pdf/report_UKWIR_9-10_17.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 two rounds the following determinands were to be measured:

- UKWIR 9/17
  - Cypermethrin
- UKWIR 10/17
  - Hexabromocyclododecane (HBCDD)

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 in µg/l
Cypermethrin	0,0004
Hexabromocyclododecane	0,0092

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 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 formulation of the spiked samples. For cypermethrin and HBCDD no matrix contents were considered.

The uncertainty of the spike was calculated from a complete uncertainty budget according to GUM.

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:

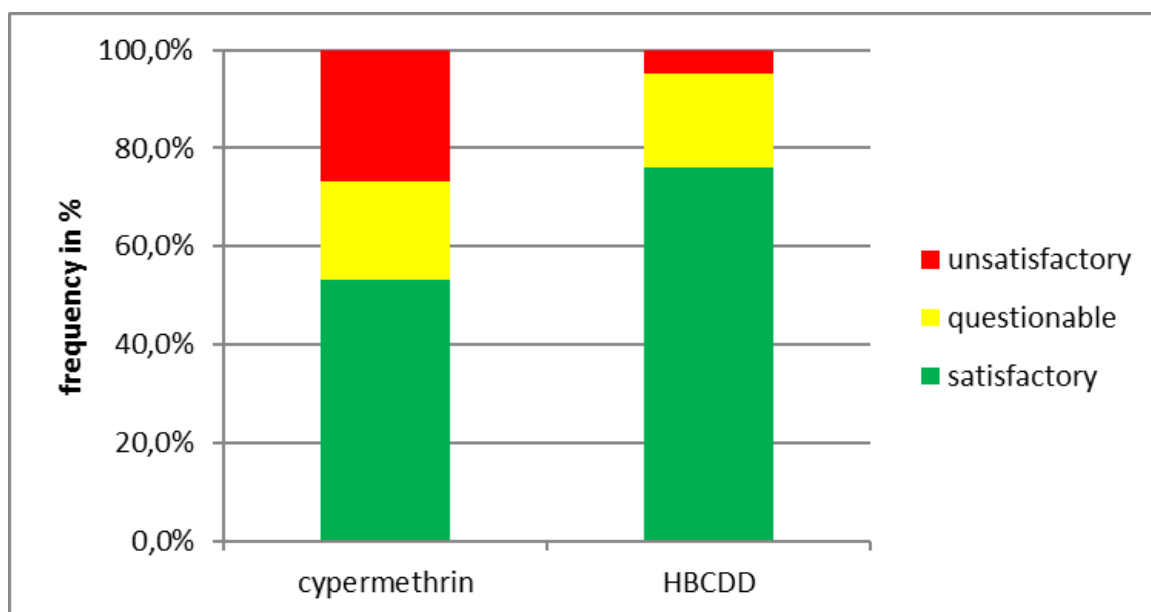
$ z  \leq 2.0$	satisfactory
$2.0 <  z  < 3.0$	questionable
$ z  \geq 3.0$	unsatisfactory

## Results of evaluation

### Number of participants:

PT round	Determinands	Number of participants	Number of participants reporting results
UKWIR 9/17	cypermethrin	6	5
UKWIR 10/17	HBCDD	8	7

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

### Mean vs. spiked amount

Here the assigned values are shown versus the spiked amount of determinand including the respective expanded uncertainties ( $k=2$ ).

### 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 9/17**

<b>cypermethrin</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	0,0010	3,44	0,0014	0,0003	25,00	0,0015	0,0005	50,00	-50,00	5	1	3	80,0
2	0,0017	3,12	0,0016	0,0004	25,00	0,0025	0,0008	50,00	-50,00	5	1	1	40,0
3	0,0021	3,16	0,0006	0,0005	25,00	0,0031	0,0010	50,00	-50,00	5	1	0	20,0
									sum	15	3	4	46,7

**Mean vs. spiked amount – relative standard deviation**

Because of the low number of participants, no robust mean was calculated from participants' data. A fixed value of 25% was used as standard deviation for proficiency assessment.

**Used methods**

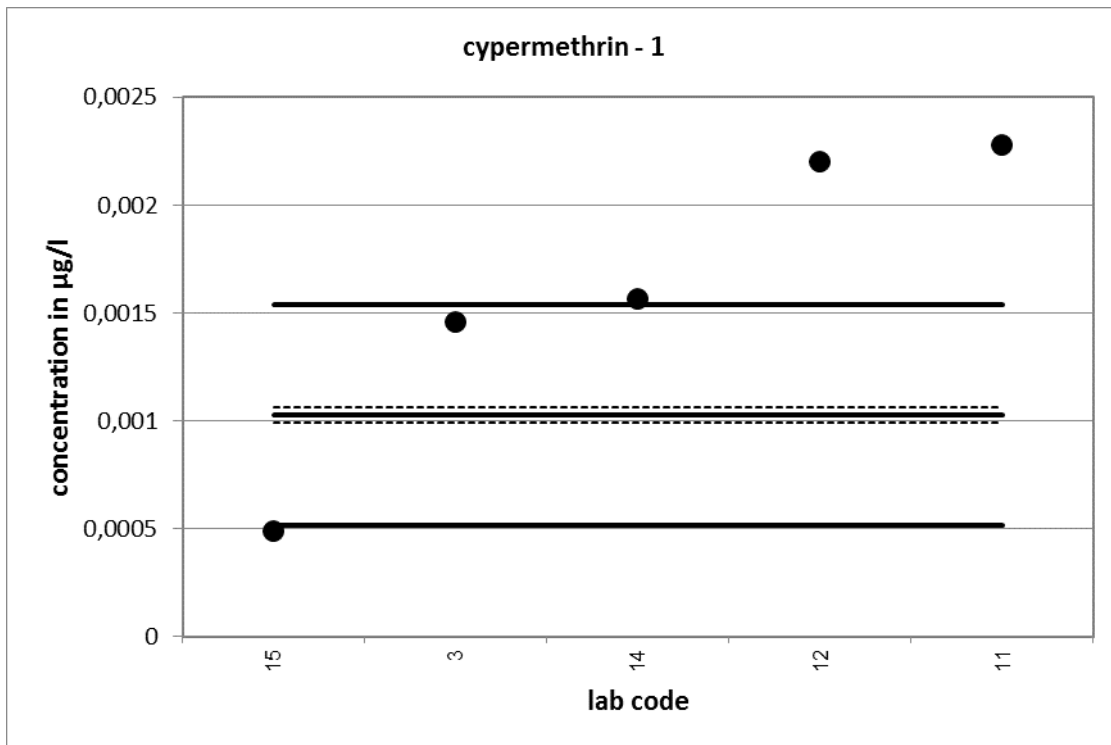
There is no comparison of the methods due to the low number of participants.

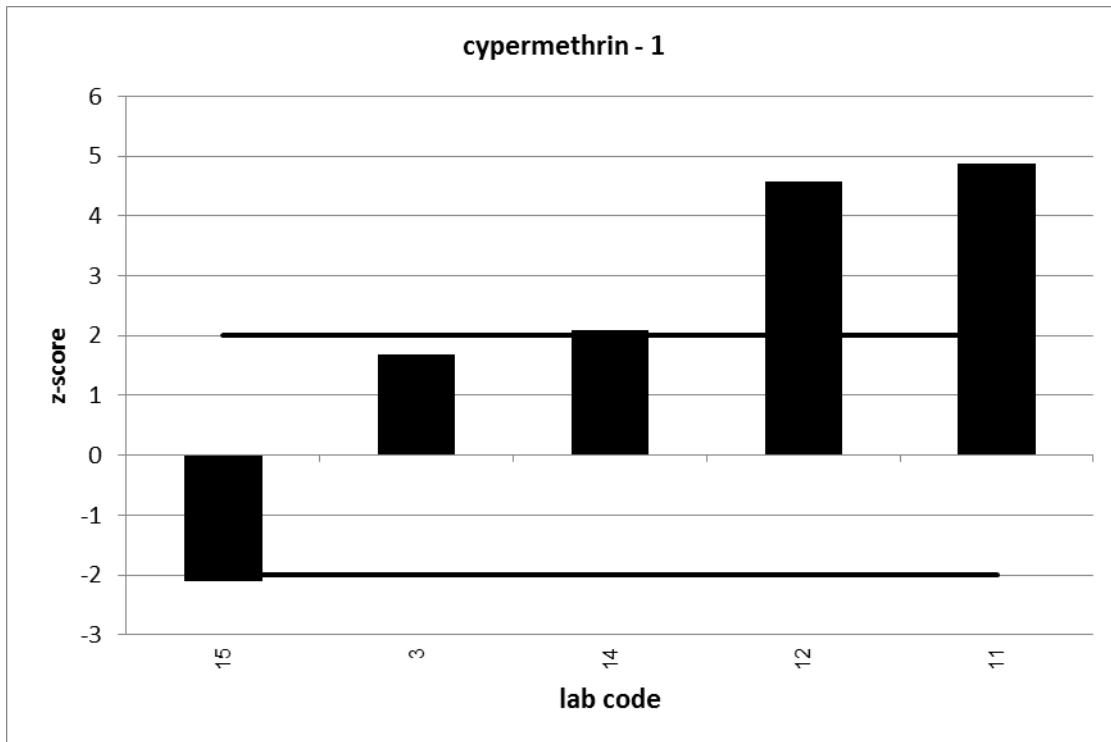


UKWIR 9/17		cypermethrin - 1			
assigned value [ $\mu\text{g/l}$ ]*		0,001027 $\pm$ 0,000035			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,00154			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,0005135			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	$\zeta$ -score	z-score	assessm.*
3	0,00146			1,7	s
11	0,00228			4,9	u
12	0,0022			4,6	u
14	0,001565			2,1	q
15	0,000489			-2,1	q

\* 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



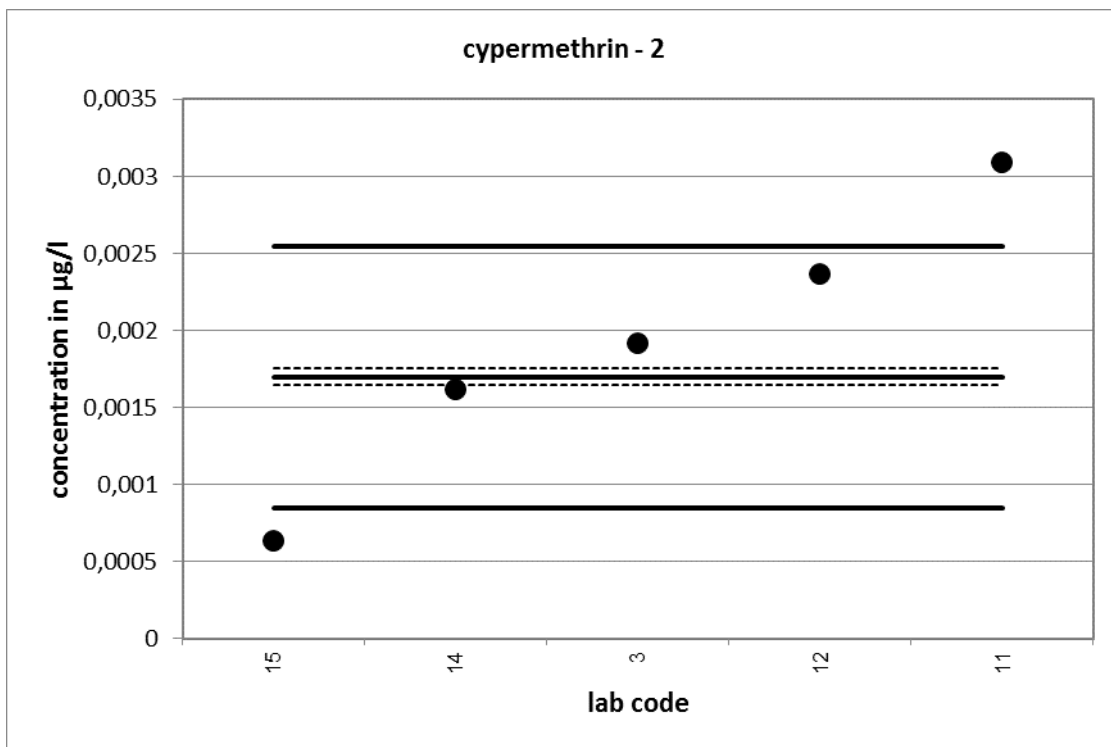


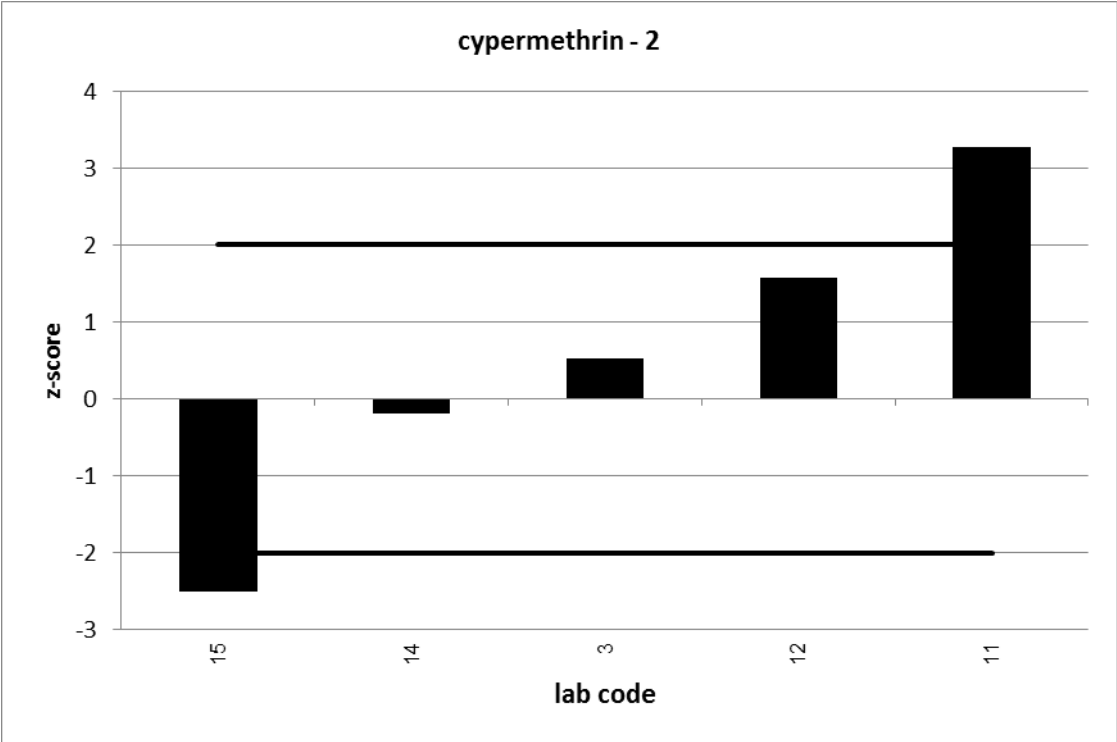
No laboratory reported measurement uncertainties.

UKWIR 9/17		cypermethrin - 2			
assigned value [ $\mu\text{g/l}$ ]*		0,001699 $\pm$ 0,000053			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,002549			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,0008497			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	$\zeta$ -score	z-score	assessm.*
3	0,00192			0,5	s
11	0,00309			3,3	u
12	0,00237			1,6	s
14	0,001616			-0,2	s
15	0,000636			-2,5	q

\* 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



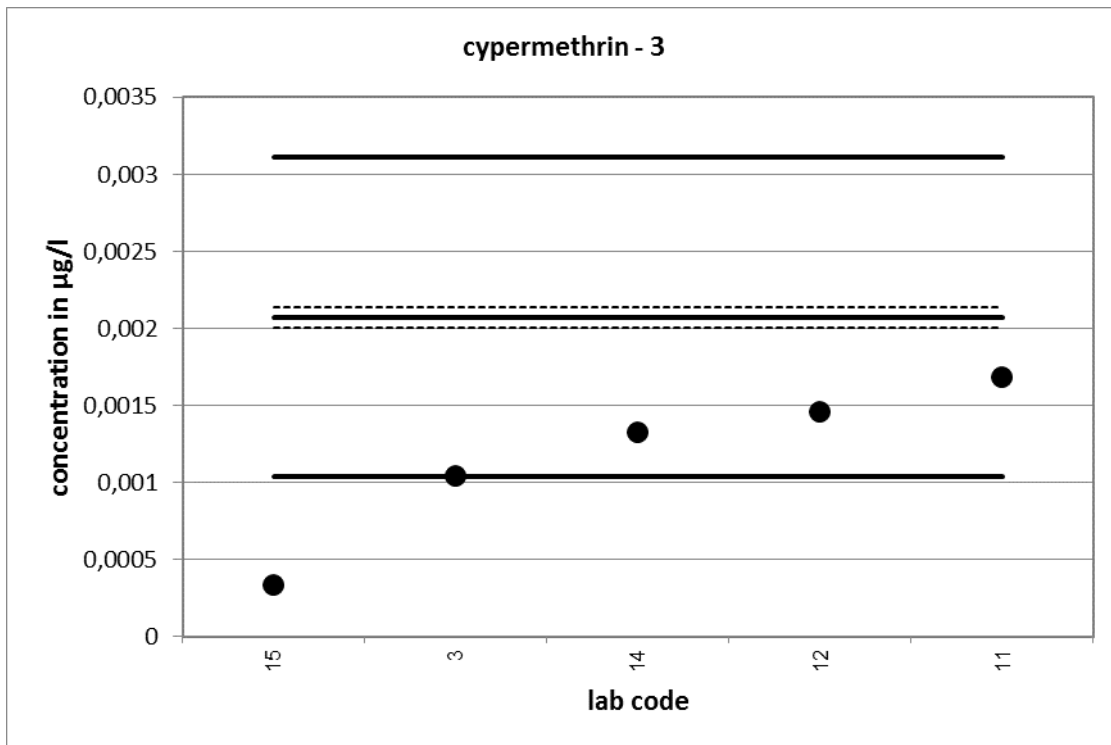


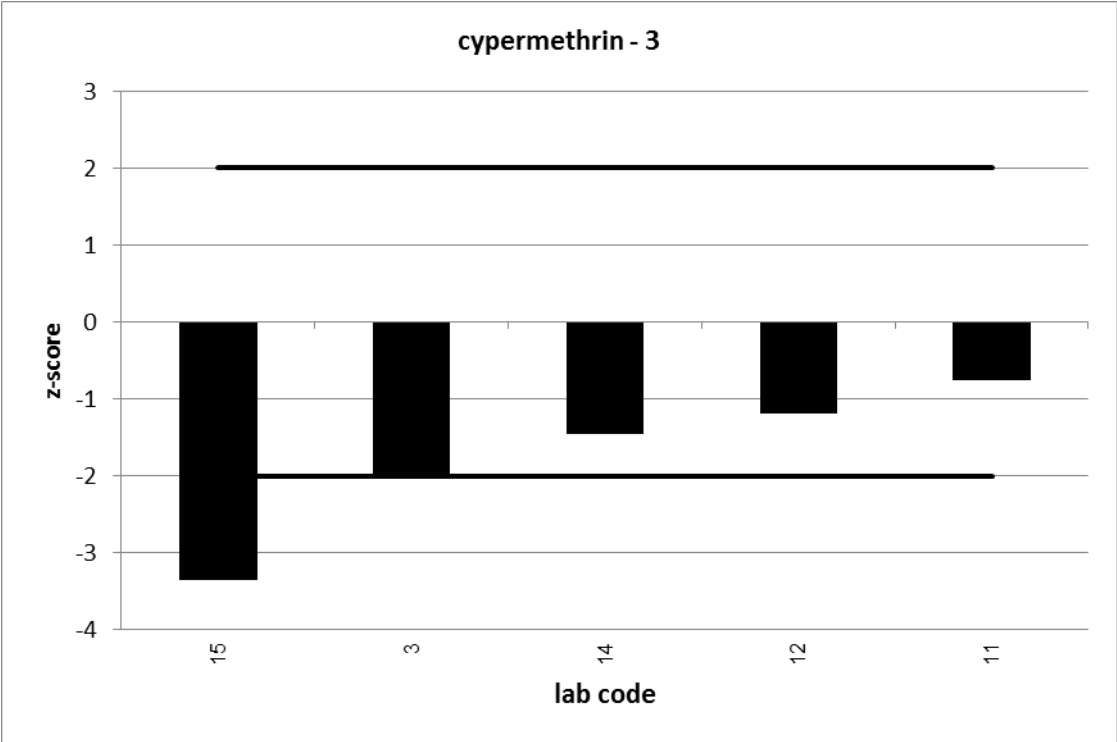
No laboratory reported measurement uncertainties.

UKWIR 9/17		cypermethrin - 3			
assigned value [ $\mu\text{g/l}$ ]*		0,002074 $\pm$ 0,000066			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,003111			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,001037			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	$\zeta$ -score	z-score	assessm.*
3	0,00104			-2,0	s
11	0,00168			-0,8	s
12	0,00146			-1,2	s
14	0,001323			-1,4	s
15	0,000331			-3,4	u

\* 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



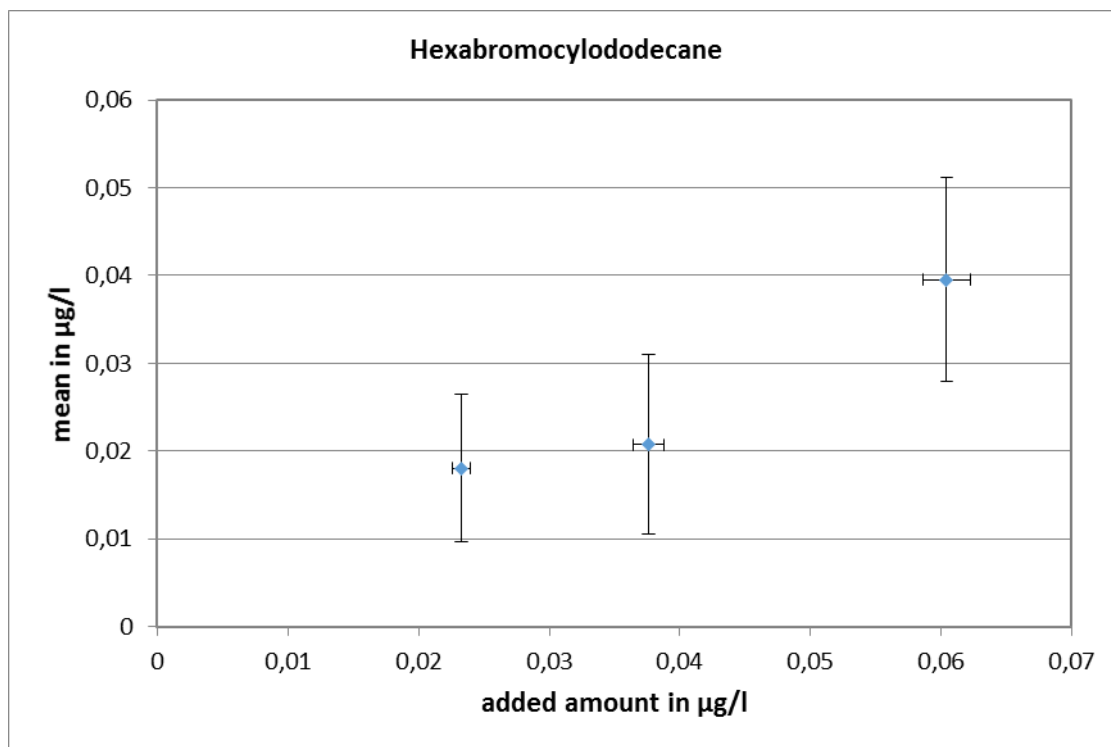


No laboratory reported measurement uncertainties.

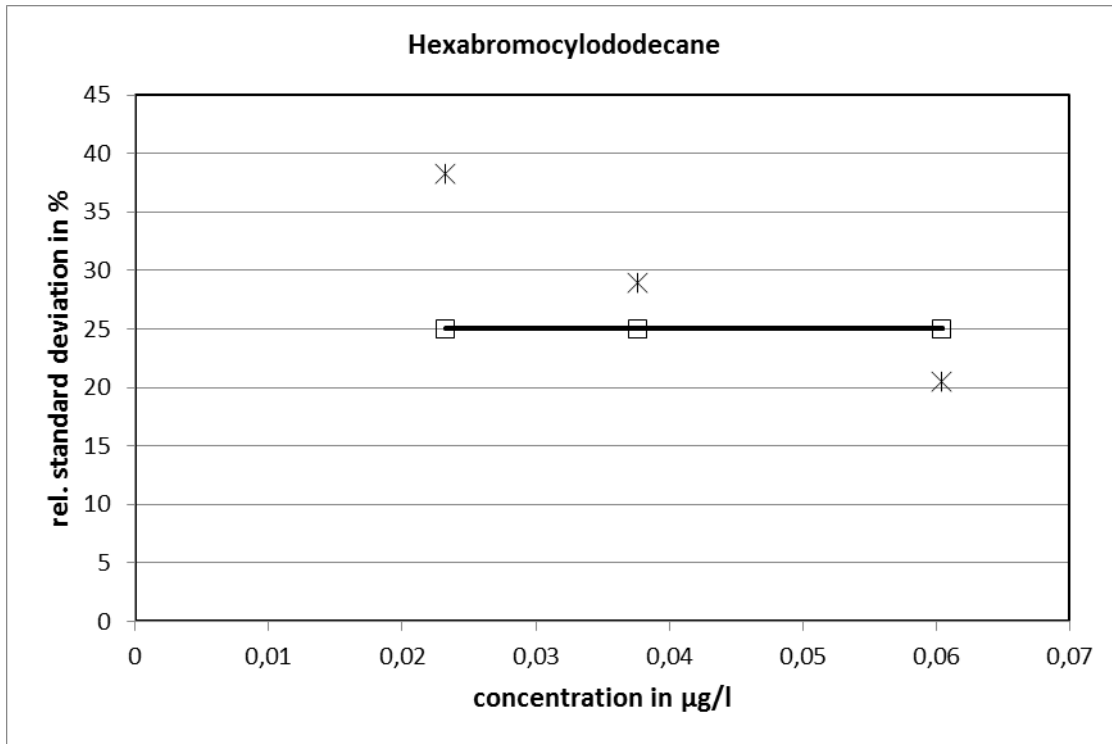
**UKWIR 10/17**

<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	0,0233	2,47	0,0089	0,0058	25,00	0,0349	0,0116	50,00	-50,00	7	1	0	14,3	
2	0,0376	2,81	0,0109	0,0094	25,00	0,0564	0,0188	50,00	-50,00	7	4	0	57,1	
3	0,0604	2,69	0,0124	0,0151	25,00	0,0906	0,0302	50,00	-50,00	7	1	0	14,3	
										sum	21	6	0	28,6

**Mean vs. spiked amount**

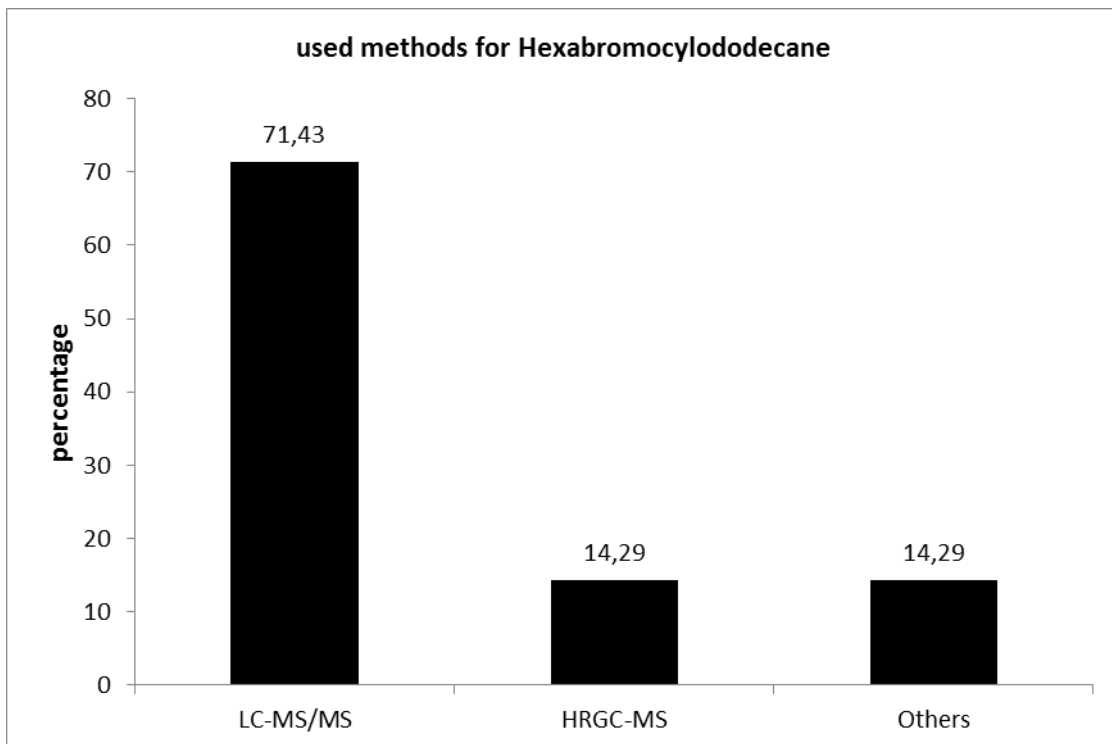


**Relative standard deviation**



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

**Used methods**

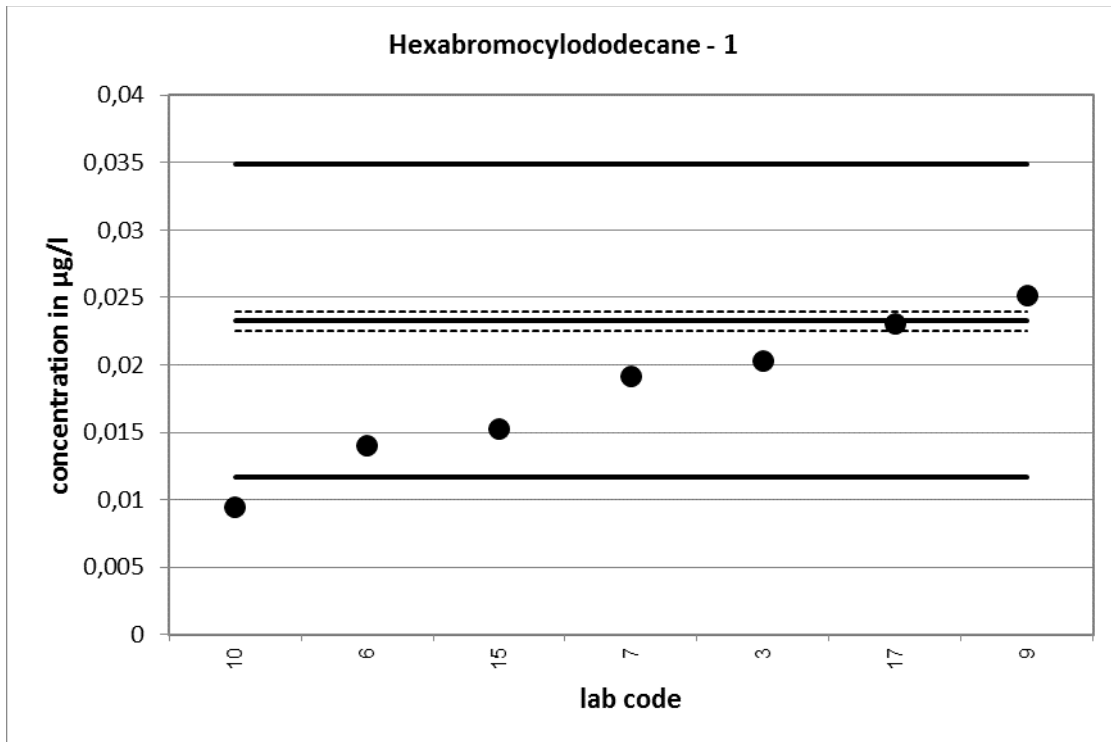


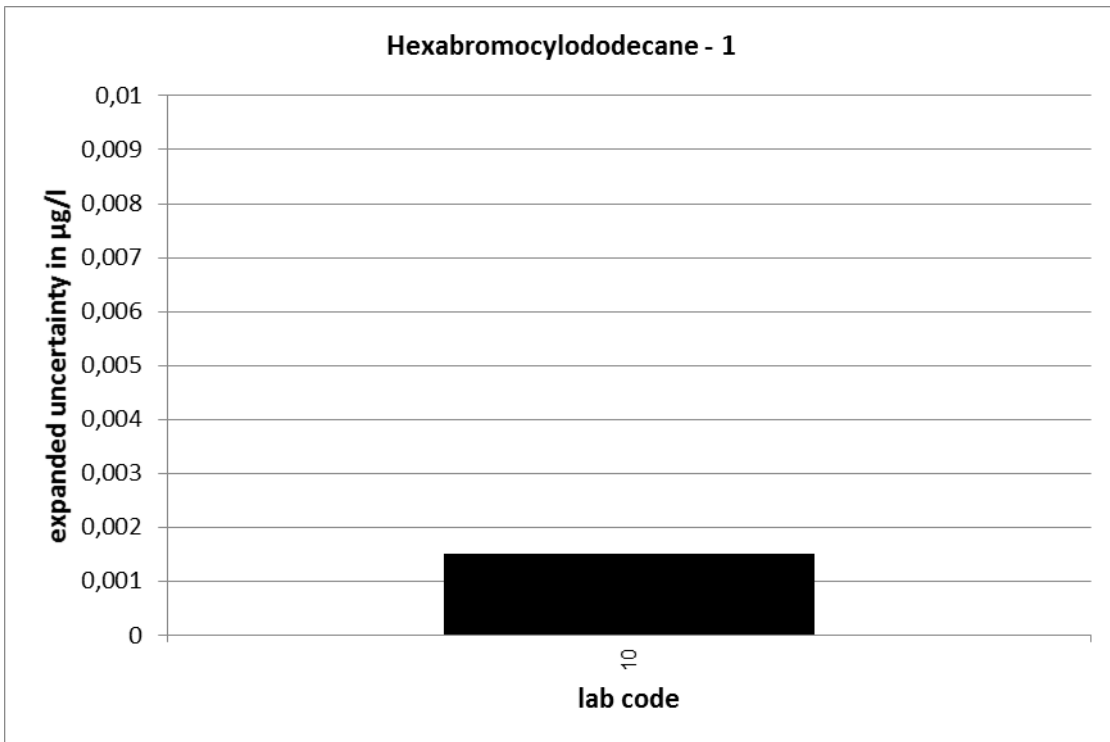
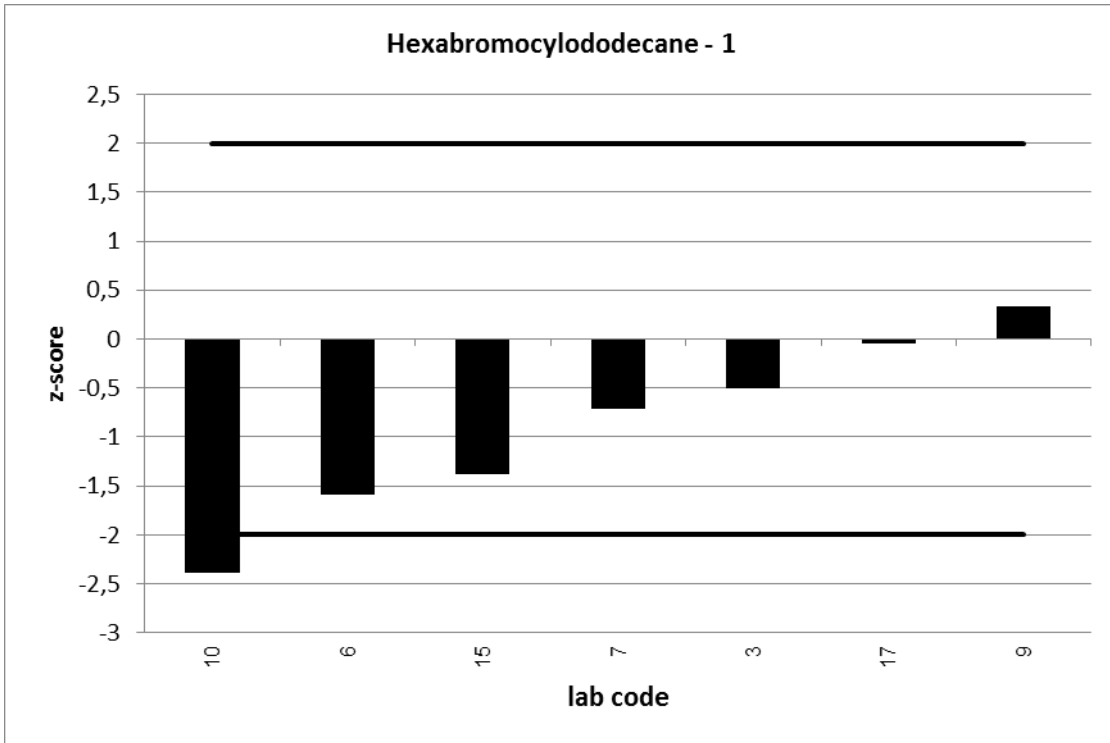


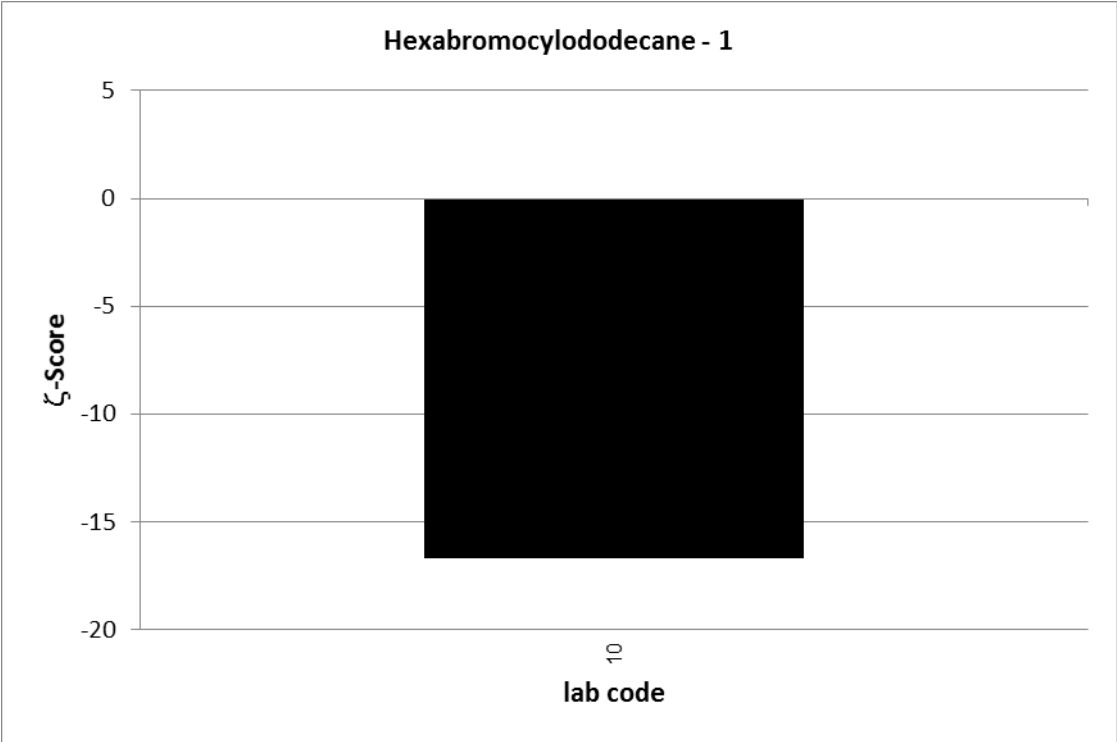
UKWIR 10/17		Hexabromocyclododecane - 1			
assigned value [ $\mu\text{g/l}$ ]*		0,02327 $\pm$ 0,00071			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,0349			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,01163			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	$\zeta$ -score	z-score	assessm.*
3	0,0203			-0,5	s
6	0,014			-1,6	s
7	0,0191			-0,7	s
9	0,02518			0,3	s
10	0,0094	0,002	-16,7	-2,4	q
15	0,0152			-1,4	s
17	0,023			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



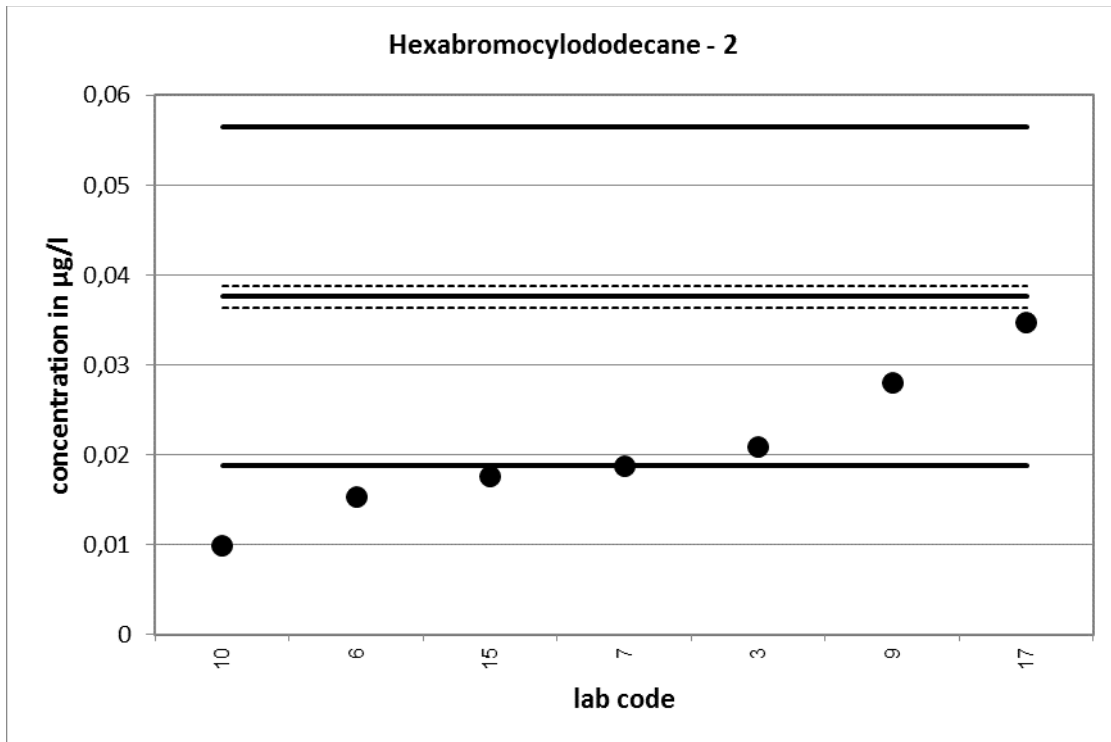


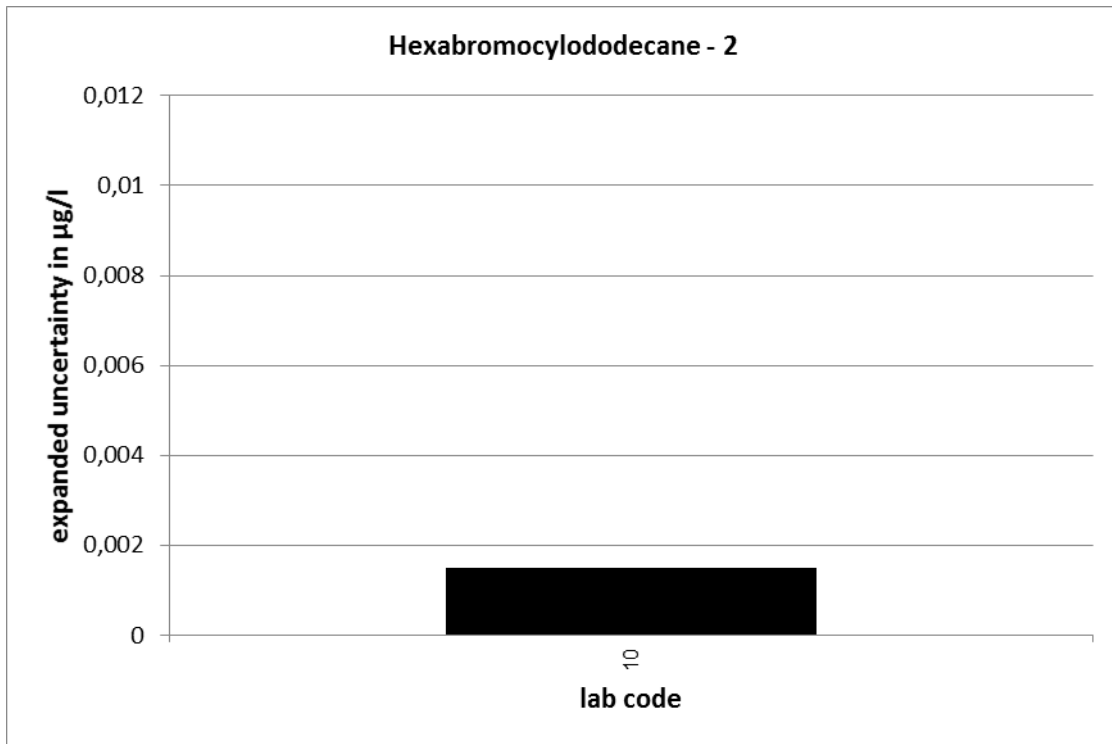


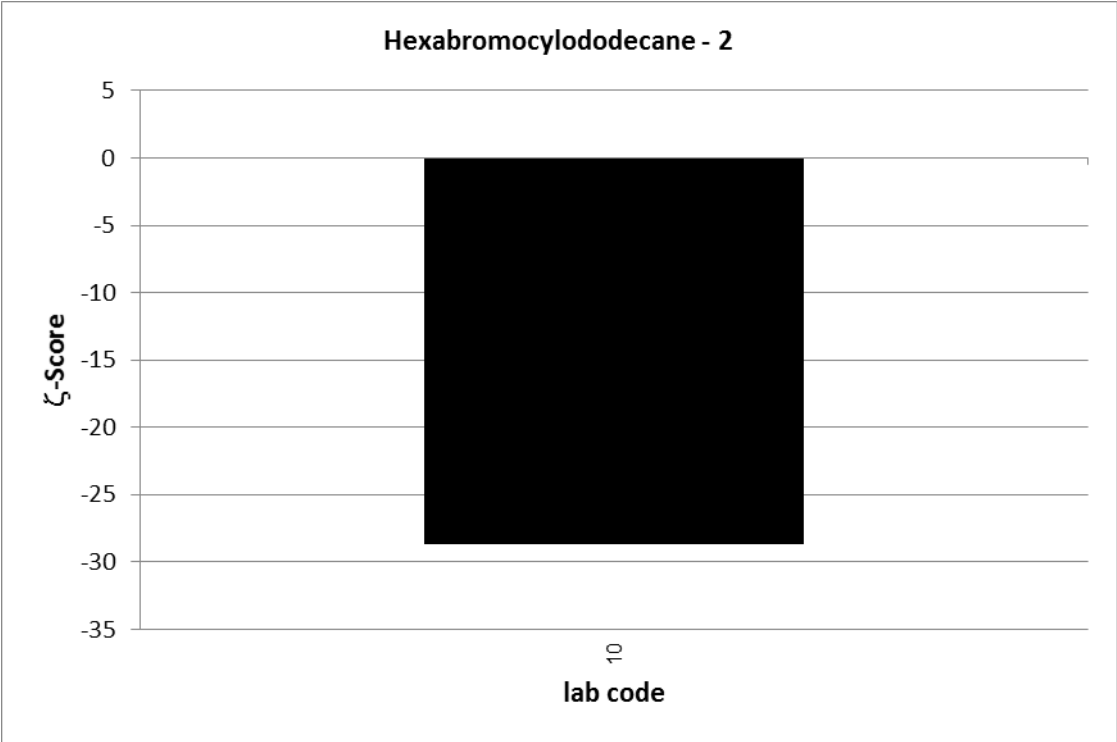
UKWIR 10/17		Hexabromocyclododecane - 2			
assigned value [ $\mu\text{g/l}$ ]*		0,0376 $\pm$ 0,00121			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,0564			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,0188			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	$\zeta$ -score	z-score	assessm.*
3	0,0209			-1,8	s
6	0,0153			-2,4	q
7	0,0187			-2,0	s
9	0,02807			-1,0	s
10	0,0099	0,002	-28,7	-2,9	q
15	0,0176			-2,1	q
17	0,0347			-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







UKWIR 10/17		Hexabromocyclododecane - 3			
assigned value [ $\mu\text{g/l}$ ]*		0,06042 $\pm$ 0,00177			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,09064			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,03021			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	$\zeta$ -score	z-score	assessm.*
3	0,0403			-1,3	s
6	0,0336			-1,8	s
7	0,0397			-1,4	s
9	0,05399			-0,4	s
10	0,0112	0,002	-42,4	-3,3	u
15	0,0376			-1,5	s
17	0,0507			-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

