

Analytische Qualitätssicherung Baden-Württemberg

Proficiency Tests UKWIR 10/21 to 14/21
priority substances in surface water -

cypermethrin, hexabromocyclododecanes, nonylphenol, octylphenol,
triclosan, tributyltin

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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: | Gertrud Joas, Cornelia Orth |

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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

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General

These PT were 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 five rounds the following determinands were to be measured:

- UKWIR 10/21
 - cypermethrin
- UKWIR 11/21
 - hexabromocyclododecanes
- UKWIR 12/21
 - nonylphenol
 - octylphenol
- UKWIR 13/21
 - triclosan
- UKWIR 14/21
 - 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:

- 3 spiked samples for the determination of the respective determinands based on a filtered surface water (for UKWIR 12/21 waste water treatment plant effluent and for UKWIR 14/21 drinking water) sample in 1000 ml glass bottles with ground glass plug.
- 1 blank sample of the filtered surface water, waste water treatment plant effluent or 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 (GoExpress). 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 |
|-------------------------|--------------|
| cypermethrin | 0.4 ng/l |
| hexabromocyclododecanes | 9.2 ng/l |
| nonylphenol | 50 ng/l |
| octylphenol | 10 ng/l |
| triclosan | 10 ng/l |
| tributyltin | 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 with three significant digits.

Evaluation procedure

The statistical evaluation was executed according to ISO 13528:2015.

Consensus means were calculated for the UKWIR 10/21 and UKWIR 11/21 PTs as well as for UKWIR 13/21 and UKWIR 14/21. For UKWIR 12/21 (nonylphenol and octylphenol) the sum of the spiked amount and the matrix content was used. The matrix content was determined from the median of the matrix measurements of the participants.

The uncertainty of the assigned value was calculated according 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

For UKWIR 12/21 the uncertainty was combined from the uncertainty of the median of the matrix measurements and the uncertainty budget of the spiking procedure.

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:

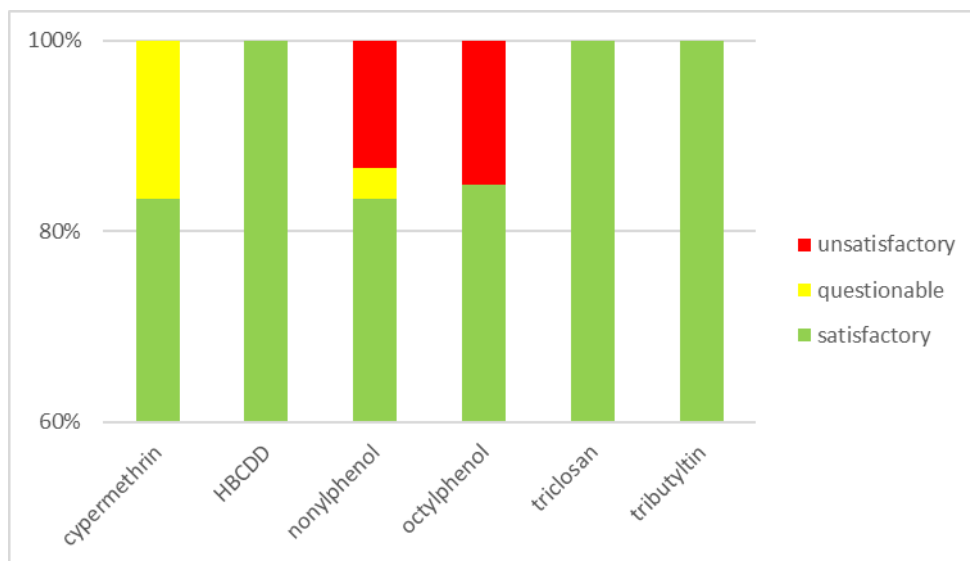
| | |
|-------------------|----------------|
| $ z \leq 2.0$ | satisfactory |
| $2.0 < z < 3.0$ | questionable |
| $ z \geq 3.0$ | unsatisfactory |

Results of evaluation

Number of participants:

| PT round | determinands | number of participants | number of participants reporting results |
|-------------|----------------------------|------------------------|--|
| UKWIR 10/21 | Cypermethrin | 4 | 4 |
| UKWIR 11/21 | hexabromocyclododecanes | 6 | 6 |
| UKWIR 12/21 | nonylphenol octylphenol | 12 | 11 |
| UKWIR 13/21 | triclosan | 10 | 9 |
| UKWIR 14/21 | tributyltin | 6 | 6 |

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 $\leq 2,0$ 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 ($z = \pm 2,0$).

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.

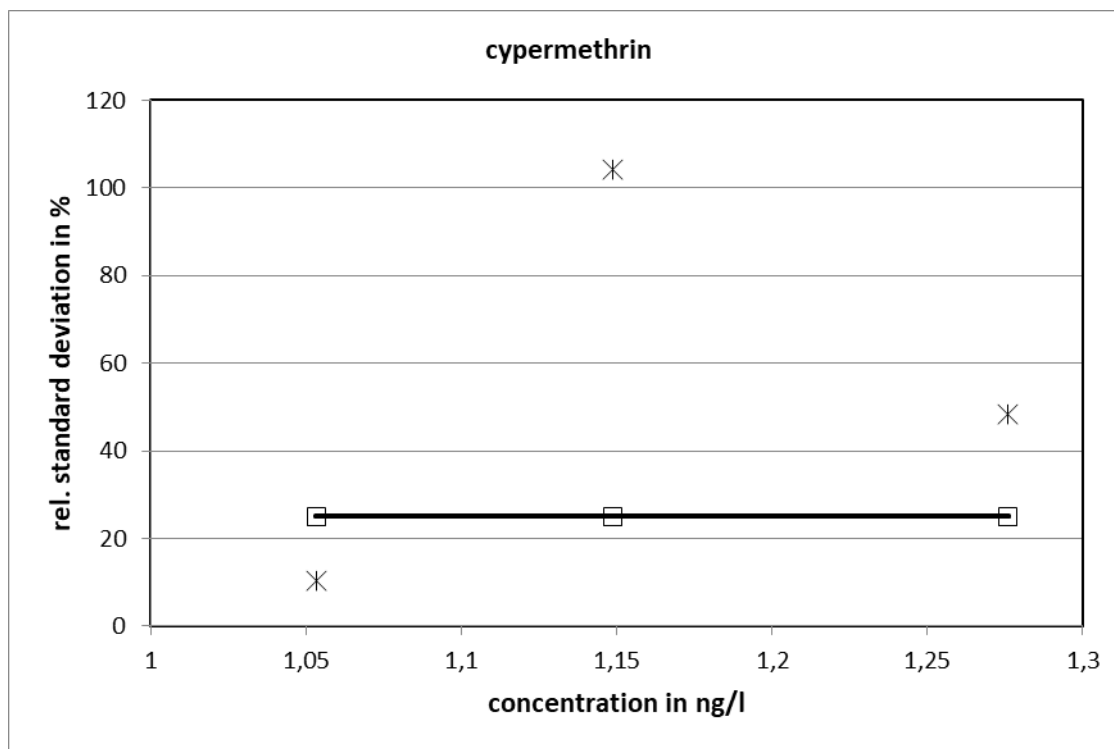
ζ -score graphs

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

UKWIR 10/21

| 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 | 1,149 | 130,40 | 1,198 | 0,2872 | 25 | 1,723 | 0,5744 | 50 | -50 | 4 | 1 | 1 | 50,0 | |
| 2 | 1,053 | 12,90 | 0,1087 | 0,2633 | 25 | 1,580 | 0,5267 | 50 | -50 | 4 | 0 | 0 | 0,0 | |
| 3 | 1,276 | 60,44 | 0,6169 | 0,3190 | 25 | 1,914 | 0,6380 | 50 | -50 | 4 | 0 | 0 | 0,0 | |
| | | | | | | | | | | sum | 12 | 1 | 1 | 16,7 |

Relative standard deviation

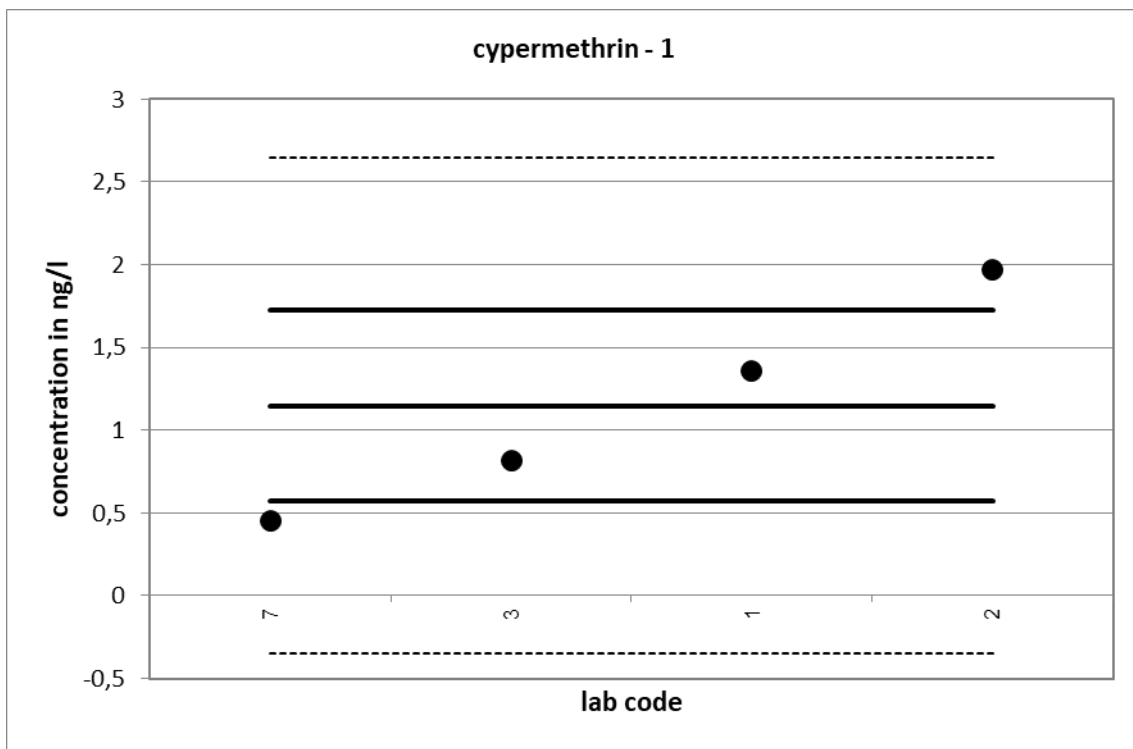


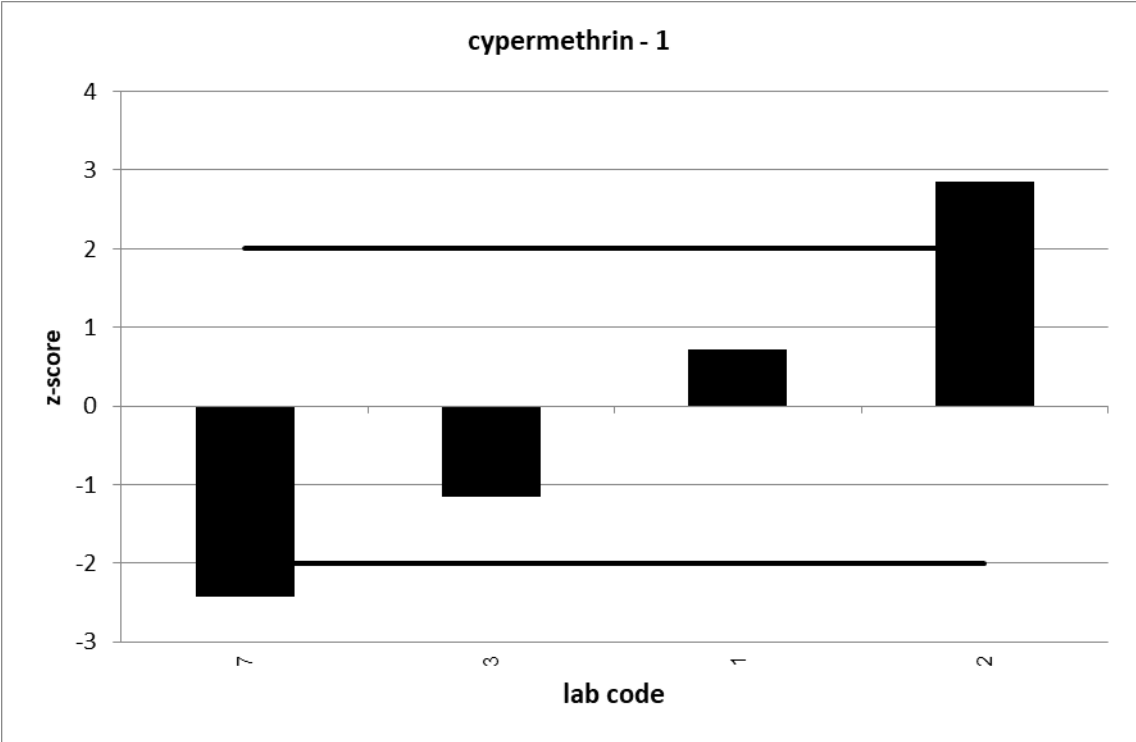
25 % is the value used as standard deviation for proficiency assessment.

| UKWIR PT 10/21 | | cypermethrin - 1 | | | |
|------------------------------|---------------|------------------|---------|---------|------------|
| assigned value [ng/l]* | | 1,149 ± 1,498 | | | |
| upper tolerance limit [ng/l] | | 1,723 | | | |
| lower tolerance limit [ng/l] | | 0,5744 | | | |
| lab code | result [ng/l] | ± | ζ-score | z-score | assessm.** |
| 1 | 1,356 | | | 0,7 | s |
| 2 | 1,97 | | | 2,9 | q |
| 3 | 0,816 | | | -1,2 | s |
| 7 | 0,453 | | | -2,4 | 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

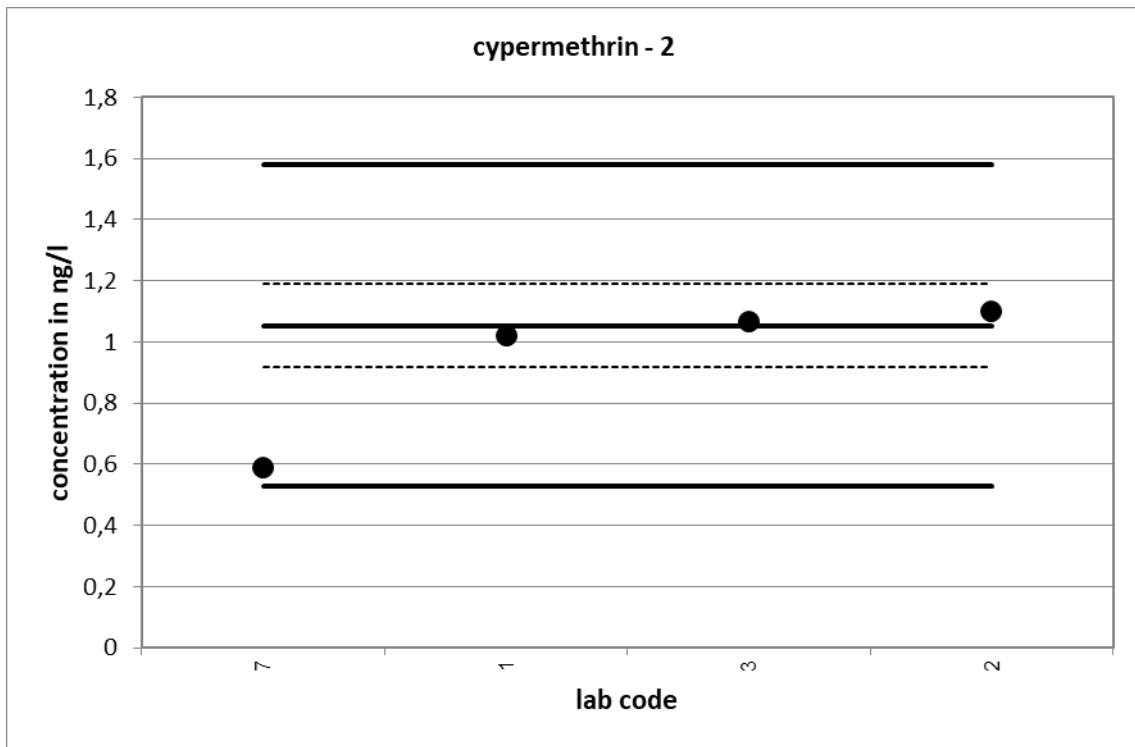


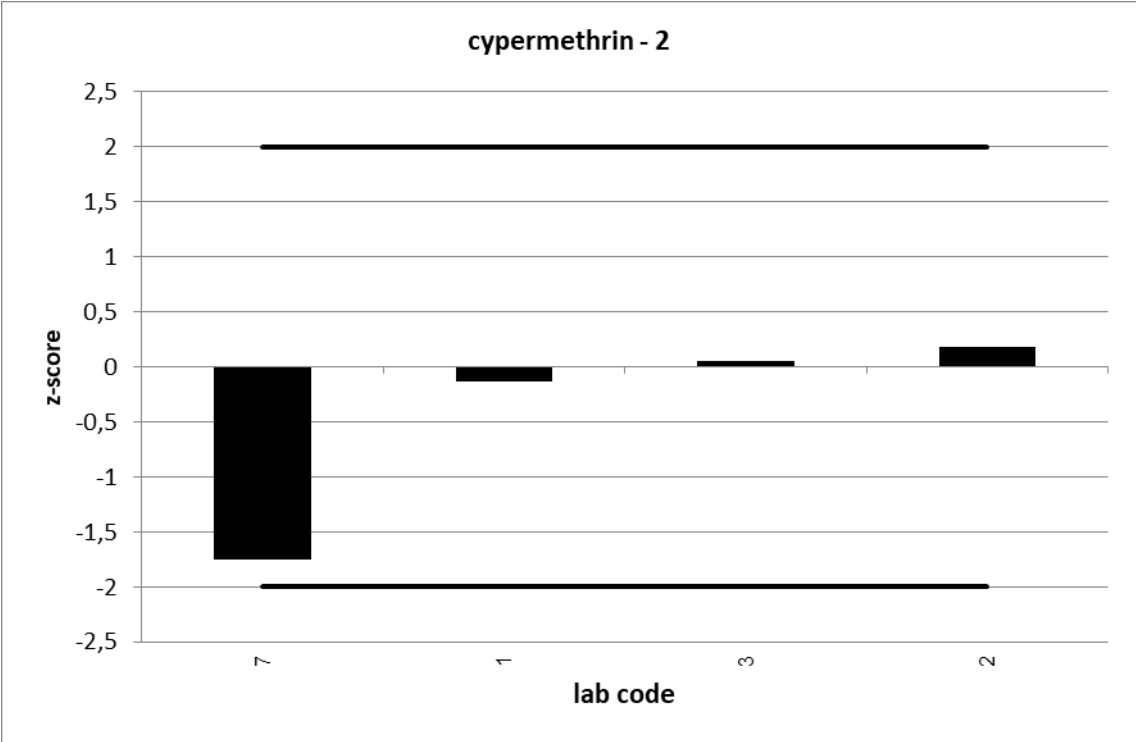


| UKWIR PT 10/21 | | cypermethrin - 2 | | | |
|------------------------------|---------------|------------------|---------|---------|------------|
| assigned value [ng/l]* | | 1,053 ± 0,136 | | | |
| upper tolerance limit [ng/l] | | 1,58 | | | |
| lower tolerance limit [ng/l] | | 0,5267 | | | |
| lab code | result [ng/l] | ± | ζ-score | z-score | assessm.** |
| 1 | 1,019 | | | -0,1 | s |
| 2 | 1,1 | | | 0,2 | s |
| 3 | 1,068 | | | 0,1 | s |
| 7 | 0,591 | | | -1,8 | 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

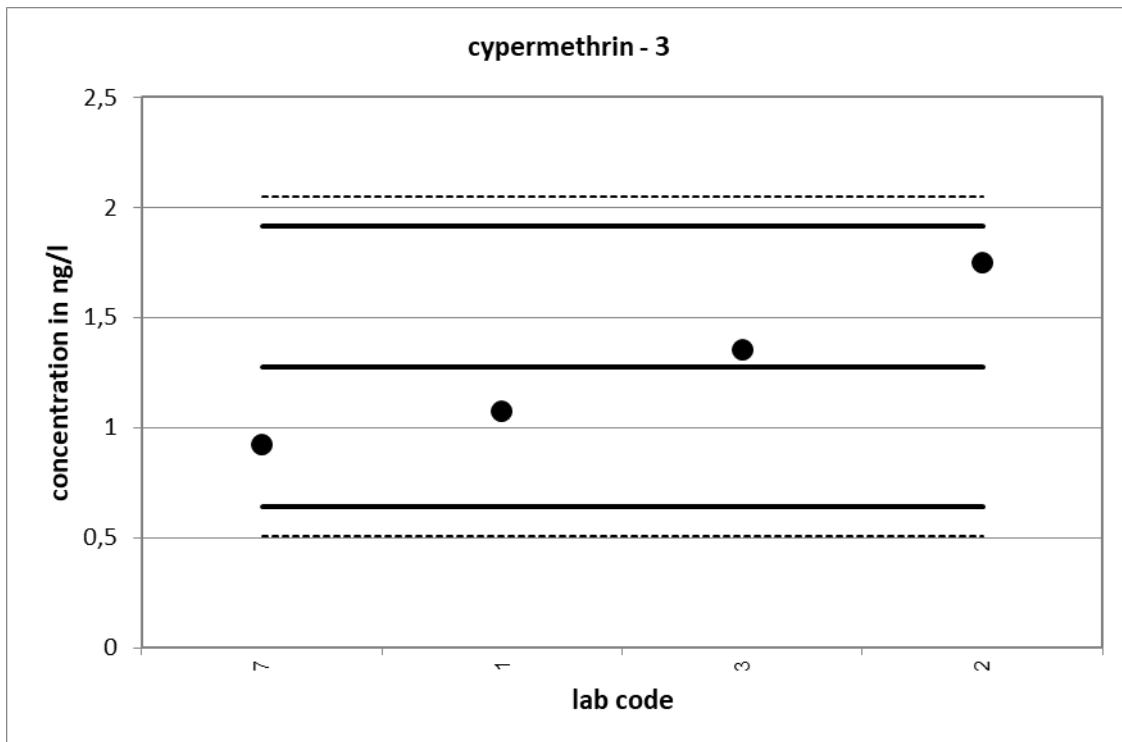


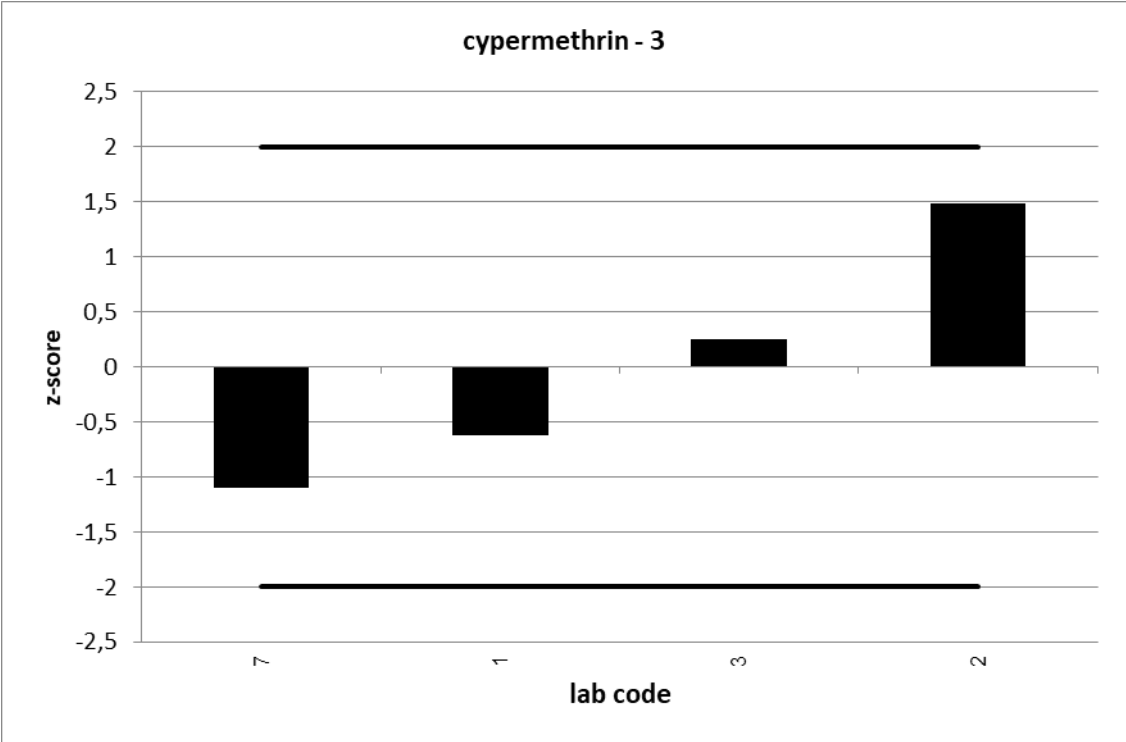


| UKWIR PT 10/21 | | cypermethrin - 3 | | | |
|------------------------------|---------------|------------------|---------|---------|------------|
| assigned value [ng/l]* | | 1,276 ± 0,771 | | | |
| upper tolerance limit [ng/l] | | 1,914 | | | |
| lower tolerance limit [ng/l] | | 0,638 | | | |
| lab code | result [ng/l] | ± | ζ-score | z-score | assessm.** |
| 1 | 1,076 | | | -0,6 | s |
| 2 | 1,75 | | | 1,5 | s |
| 3 | 1,354 | | | 0,2 | s |
| 7 | 0,924 | | | -1,1 | 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

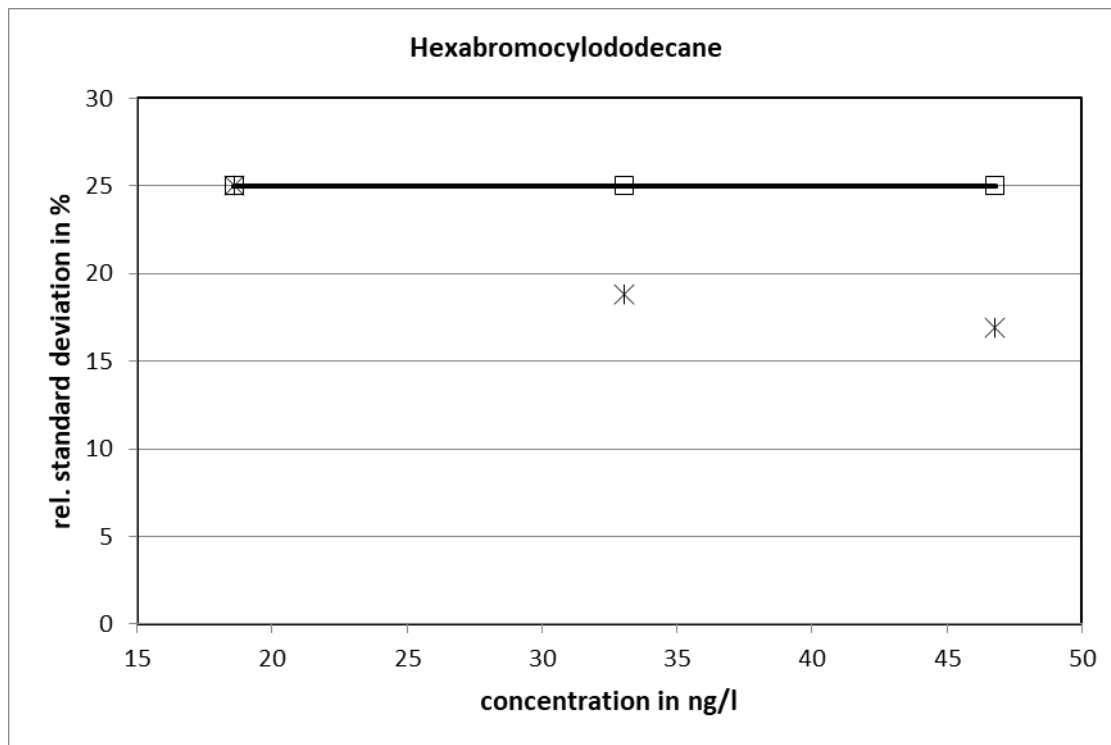




UKWIR 11/21

| Hexabromocyclododecane | | | | | | | | | | | | | |
|-------------------------------|-----------------------|--|---|--|---|------------------------------|------------------------------|---------------------------|---------------------------|-------------------|-----------|-----------|---------|
| 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 | 18,59 | 25,56 | 4,655 | 4,647 | 25,00 | 27,88 | 9,294 | 50,00 | -50,00 | 6 | 0 | 0 | 0,0 |
| 2 | 33,03 | 19,23 | 6,222 | 8,258 | 25,00 | 49,55 | 16,52 | 50,00 | -50,00 | 6 | 0 | 0 | 0,0 |
| 3 | 46,79 | 17,27 | 7,918 | 11,70 | 25,00 | 70,19 | 23,40 | 50,00 | -50,00 | 6 | 0 | 0 | 0,0 |
| | | | | | | | | | | sum | 18 | 0 | 0,0 |

Relative standard deviation

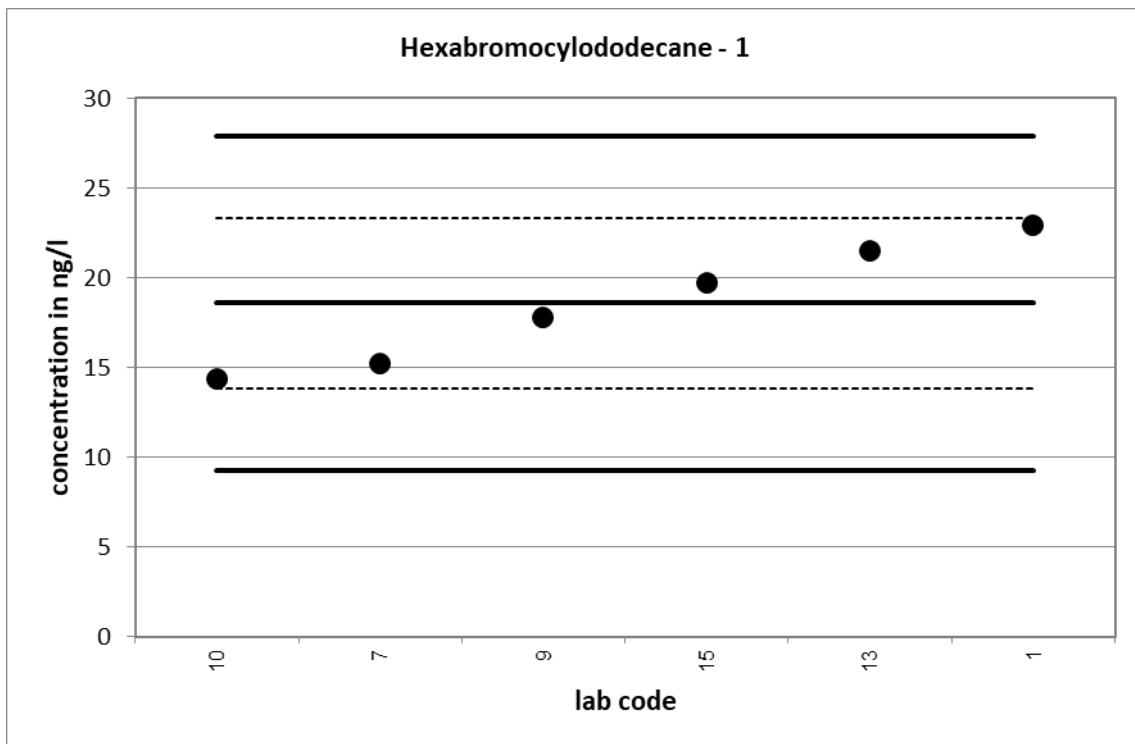


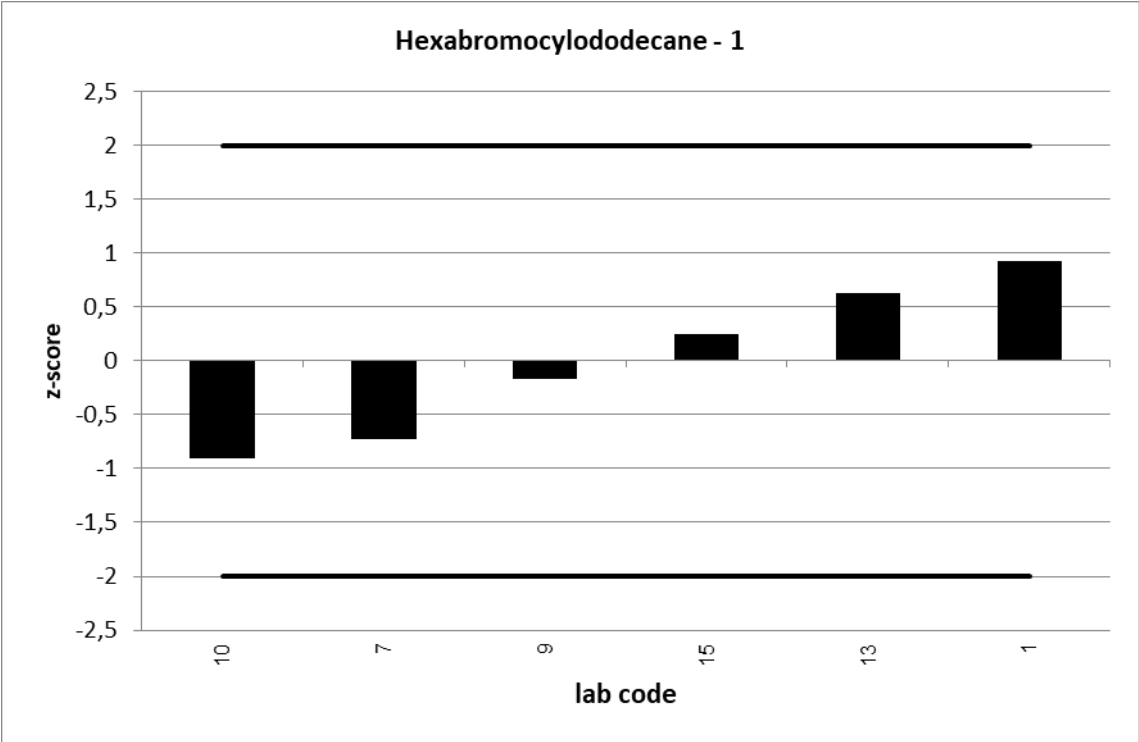
25 % is the value used as standard deviation for proficiency assessment.

| UKWIR PT 11/21 | | Hexabromocyclododecane - 1 | | | |
|------------------------------|---------------|----------------------------|---------|---------|------------|
| assigned value [ng/l]* | | 18,59 ± 4,75 | | | |
| upper tolerance limit [ng/l] | | 27,88 | | | |
| lower tolerance limit [ng/l] | | 9,294 | | | |
| lab code | result [ng/l] | ± | ζ-score | z-score | assessm.** |
| 1 | 22,9 | | | 0,9 | s |
| 7 | 15,2 | | | -0,7 | s |
| 9 | 17,8 | | | -0,2 | s |
| 10 | 14,4 | | | -0,9 | s |
| 13 | 21,5 | | | 0,6 | s |
| 15 | 19,73 | | | 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

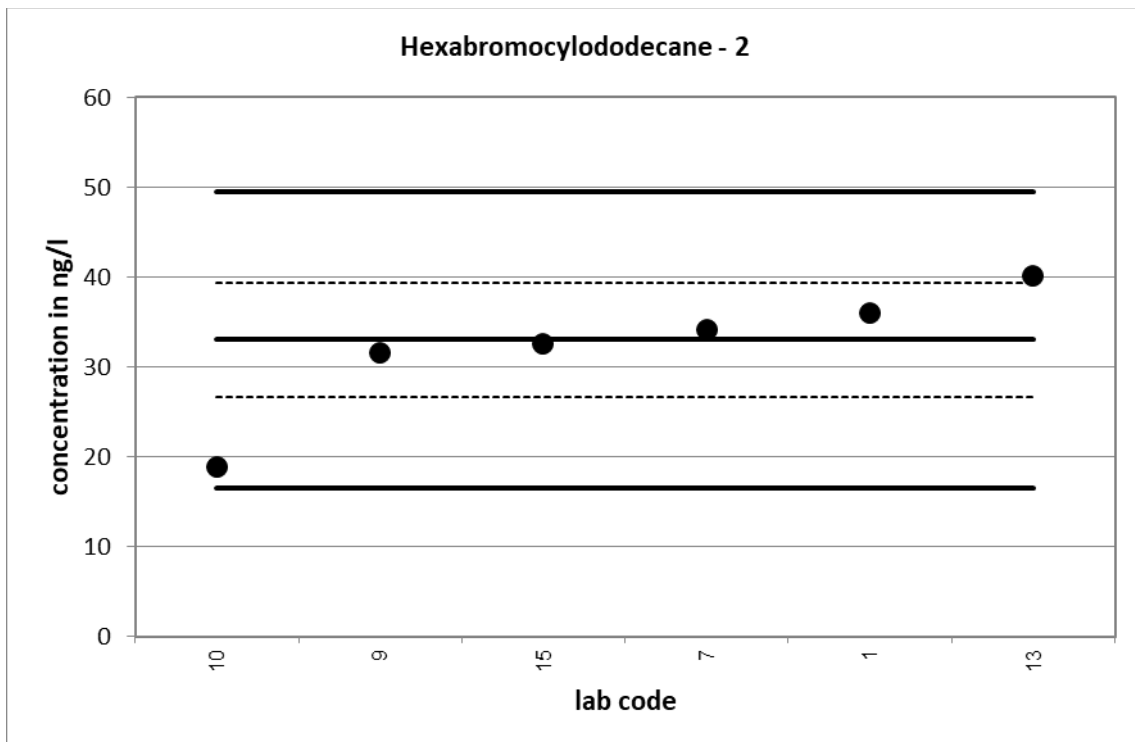


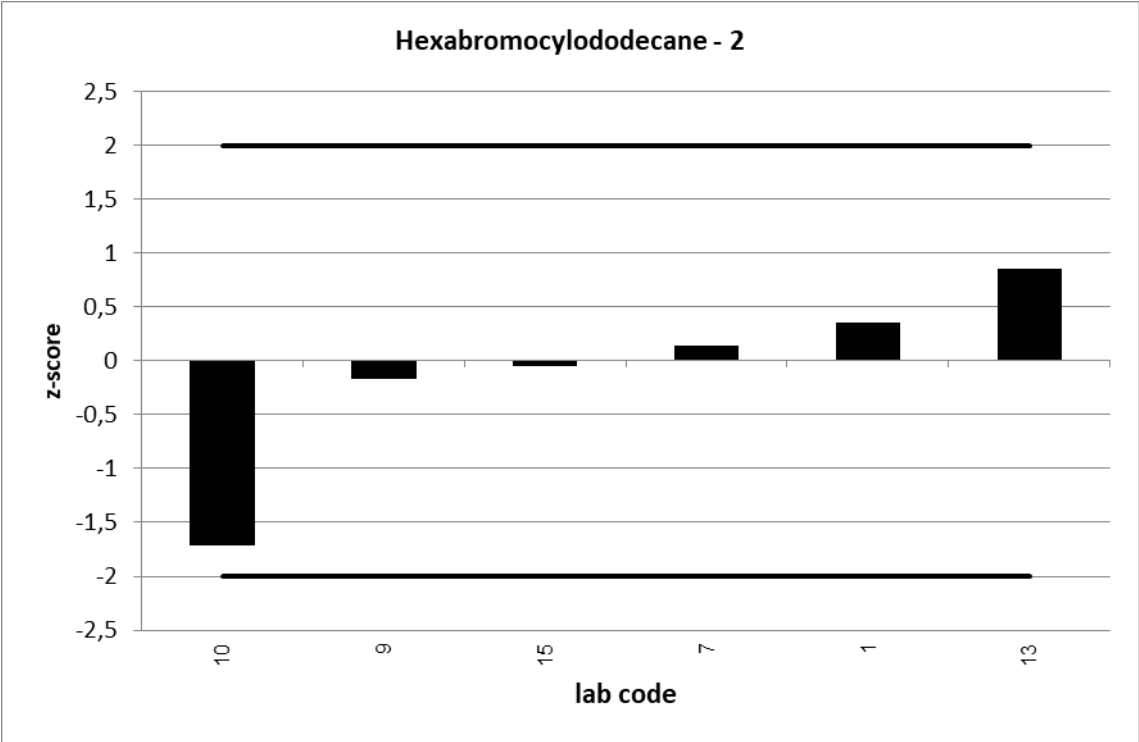


| UKWIR PT 11/21 | | Hexabromocyclododecane - 2 | | | |
|------------------------------|---------------|----------------------------|---------|---------|------------|
| assigned value [ng/l]* | | 33,03 ± 6,35 | | | |
| upper tolerance limit [ng/l] | | 49,55 | | | |
| lower tolerance limit [ng/l] | | 16,52 | | | |
| lab code | result [ng/l] | ± | ζ-score | z-score | assessm.** |
| 1 | 36 | | | 0,4 | s |
| 7 | 34,2 | | | 0,1 | s |
| 9 | 31,6 | | | -0,2 | s |
| 10 | 18,9 | | | -1,7 | s |
| 13 | 40,1 | | | 0,9 | s |
| 15 | 32,585 | | | -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

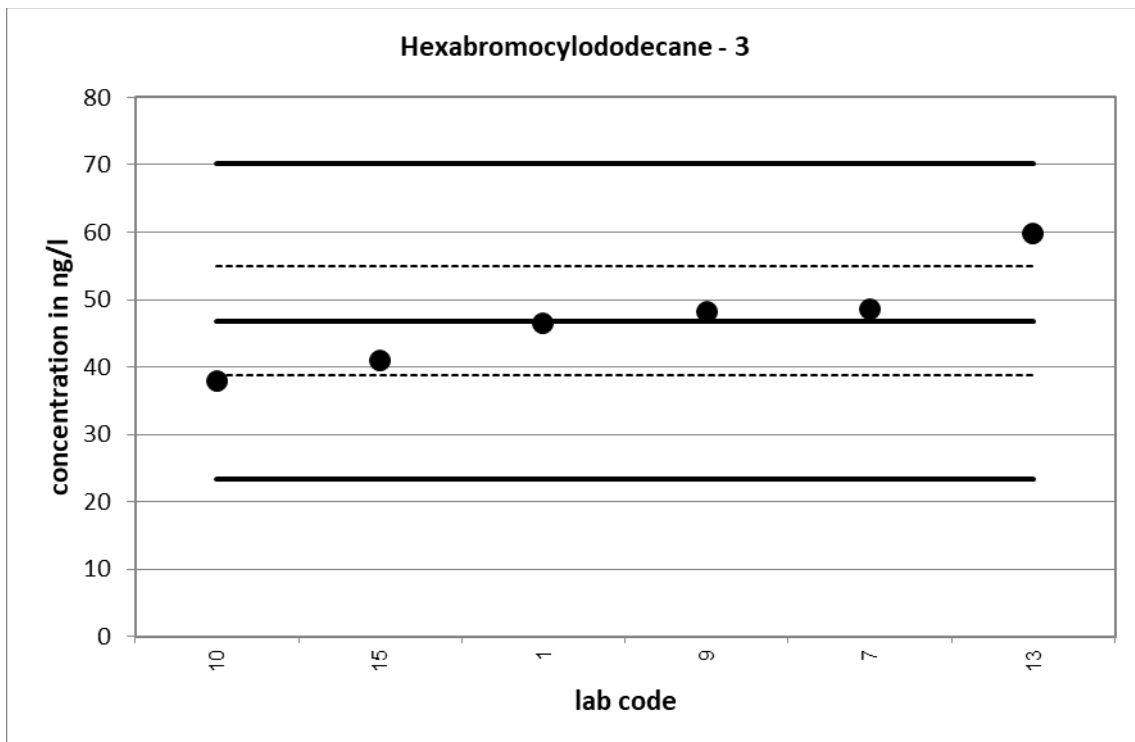


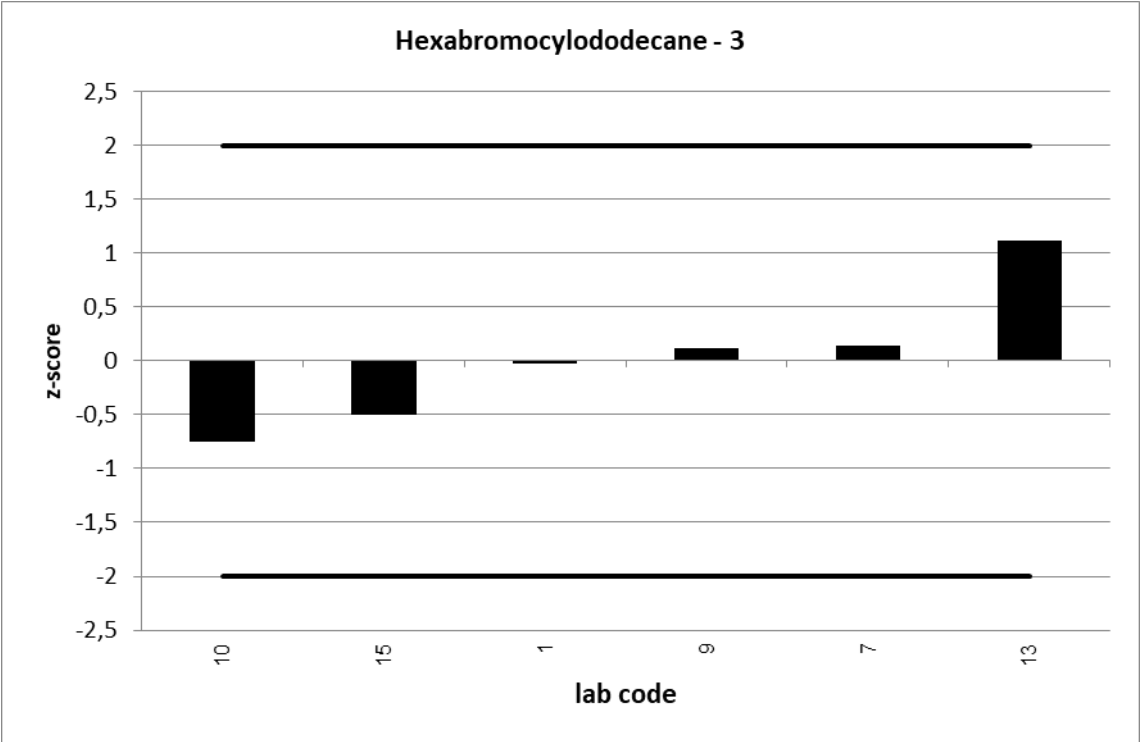


| UKWIR PT 11/21 | | Hexabromocyclododecane - 3 | | | |
|------------------------------|---------------|----------------------------|---------|---------|------------|
| assigned value [ng/l]* | | 46,79 ± 8,08 | | | |
| upper tolerance limit [ng/l] | | 70,19 | | | |
| lower tolerance limit [ng/l] | | 23,4 | | | |
| lab code | result [ng/l] | ± | ζ-score | z-score | assessm.** |
| 1 | 46,5 | | | 0,0 | s |
| 7 | 48,5 | | | 0,1 | s |
| 9 | 48,2 | | | 0,1 | s |
| 10 | 38 | | | -0,8 | s |
| 13 | 59,9 | | | 1,1 | s |
| 15 | 40,886 | | | -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

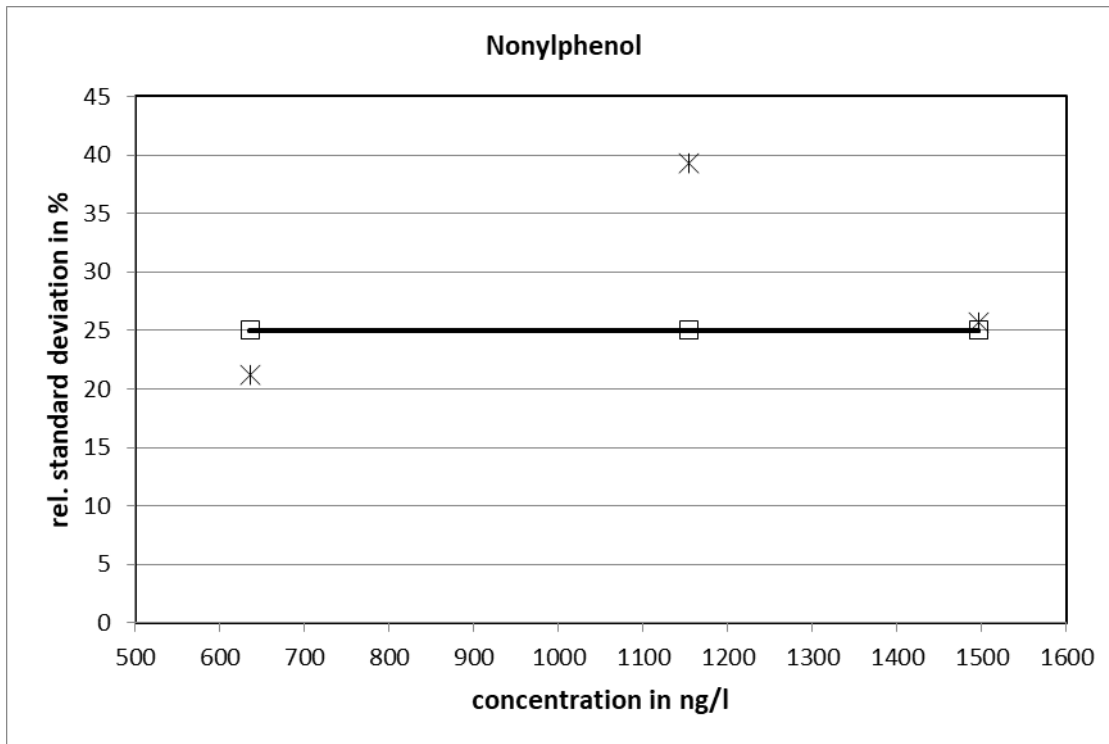




UKWIR 12/21:

| Nonylphenol | | | | | | | | | | | | | |
|--------------------|-----------------------|--|---|--|---|------------------------------|------------------------------|---------------------------|---------------------------|-------------------|-----------|-----------|---------|
| 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 | 635,4 | 15,59 | 135,0 | 158,9 | 25 | 953,2 | 317,7 | 50 | -50 | 8 | 1 | 1 | 20,0 |
| 2 | 1154 | 8,65 | 453,8 | 288,5 | 25 | 1731 | 576,9 | 50 | -50 | 9 | 1 | 0 | 10,0 |
| 3 | 1497 | 6,74 | 383,9 | 374,1 | 25 | 2245 | 748,3 | 50 | -50 | 9 | 1 | 0 | 10,0 |
| | | | | | | | | | | sum | 26 | 3 | 15,4 |

Relative standard deviation

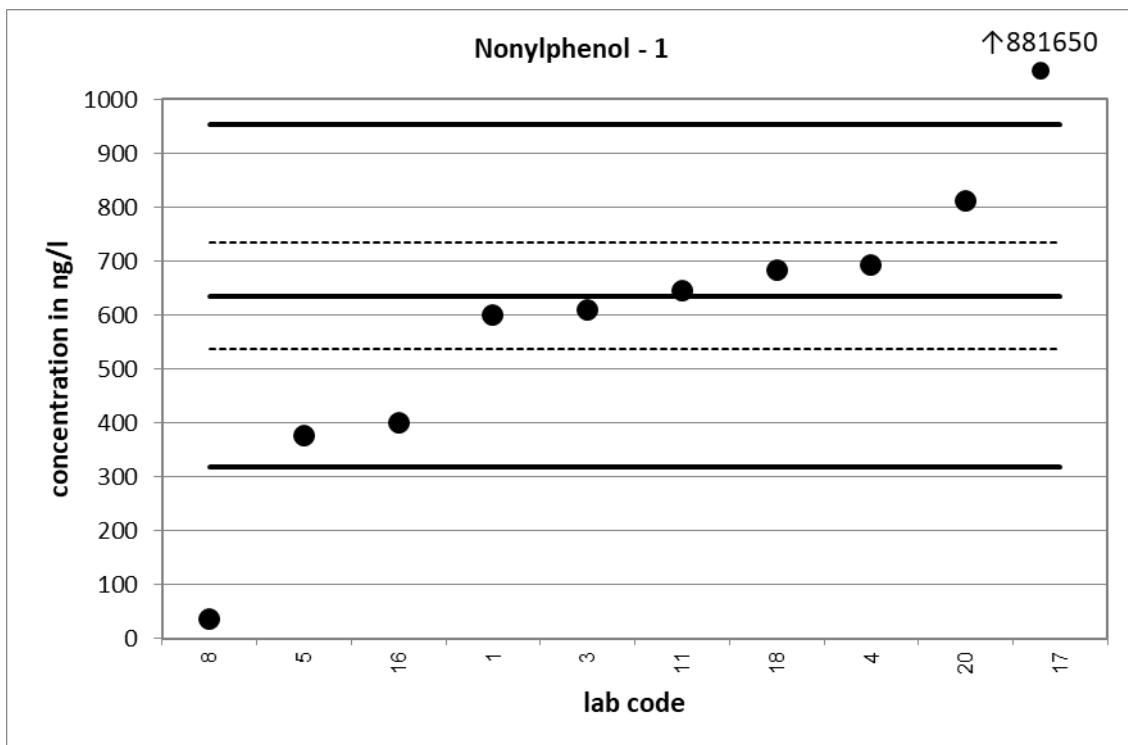


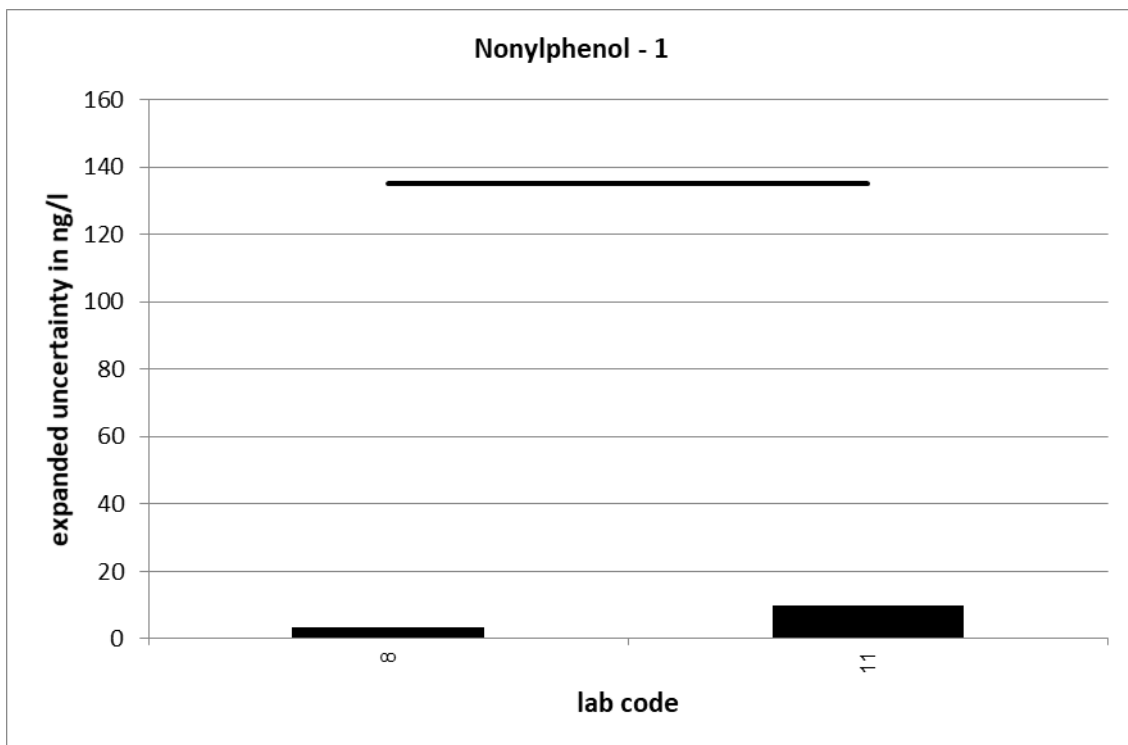
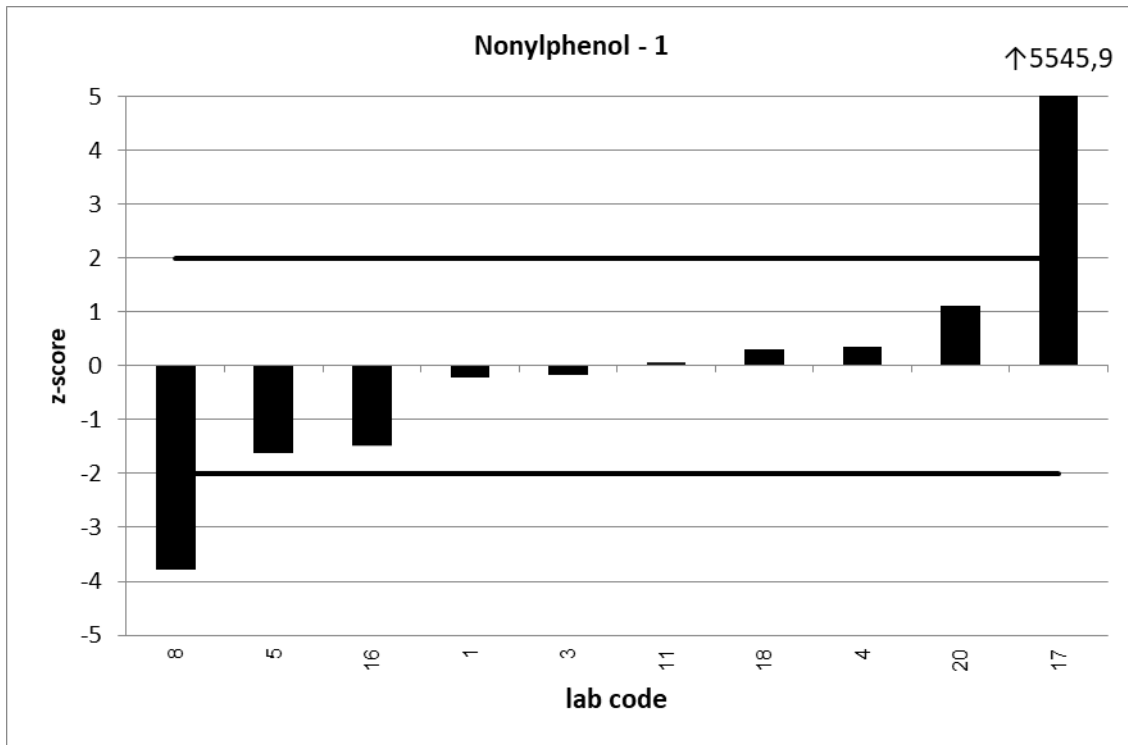
25 % is used as standard deviation for proficiency assessment.

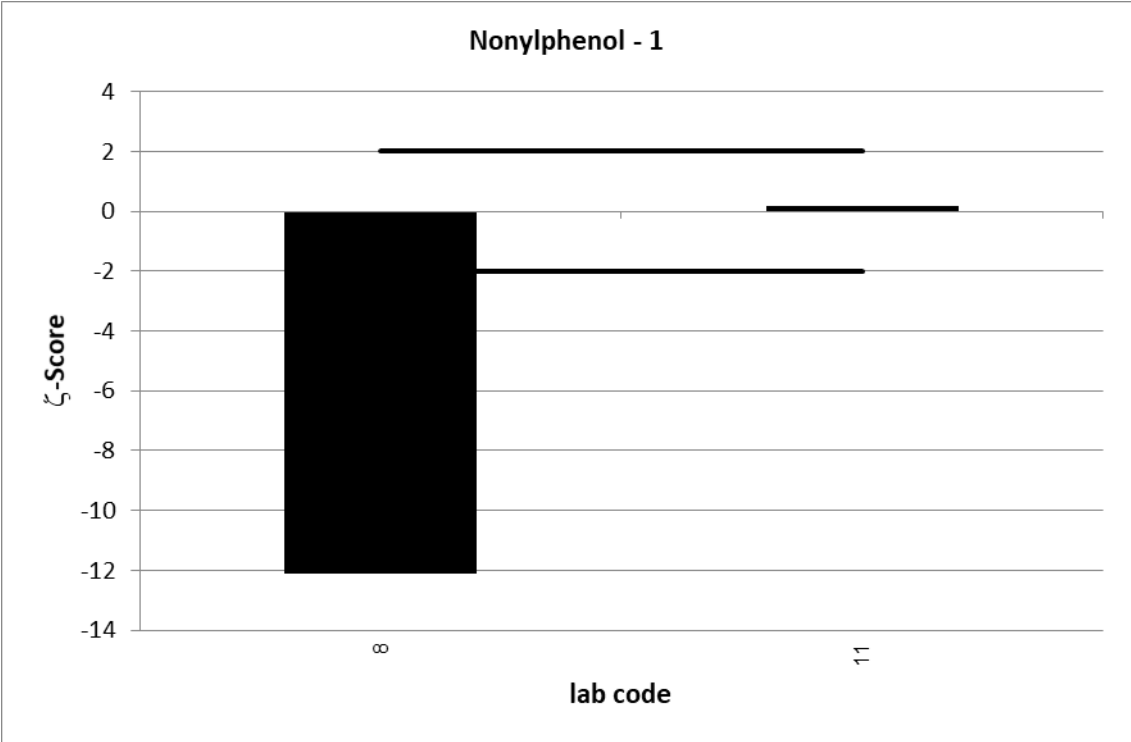
| UKWIR PT 12/21 | | Nonylphenol - 1 | | | |
|------------------------------|---------------|-----------------|---------|---------|------------|
| assigned value [ng/l]* | | 635,4 ± 99,1 | | | |
| upper tolerance limit [ng/l] | | 953,2 | | | |
| lower tolerance limit [ng/l] | | 317,7 | | | |
| lab code | result [ng/l] | ± | ζ-score | z-score | assessm.** |
| 1 | 600 | | | -0,2 | s |
| 3 | 610 | | | -0,2 | s |
| 4 | 692,7 | | | 0,4 | s |
| 5 | 377 | | | -1,6 | s |
| 8 | 35,8 | 3,58 | -12,1 | -3,8 | u |
| 11 | 645 | 10 | 0,2 | 0,1 | s |
| 16 | 400 | | | -1,5 | s |
| 17 | 881650 | | | 5545,9 | u |
| 18 | 684 | | | 0,3 | s |
| 20 | 812 | | | 1,1 | 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



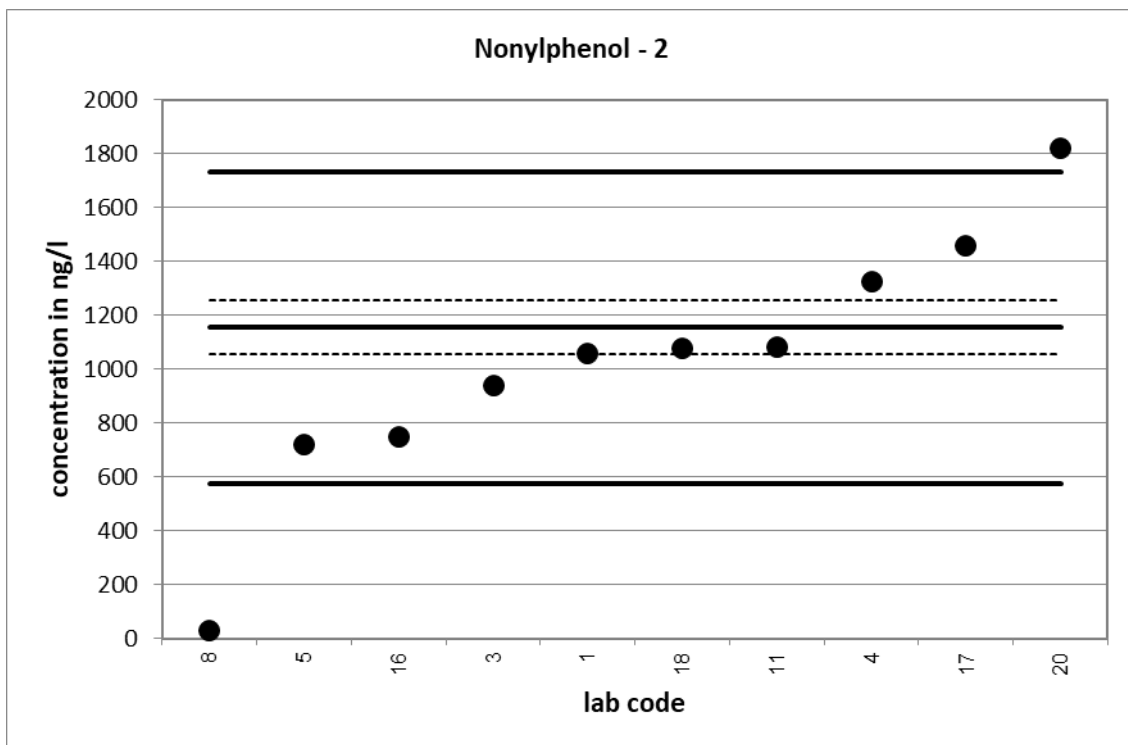


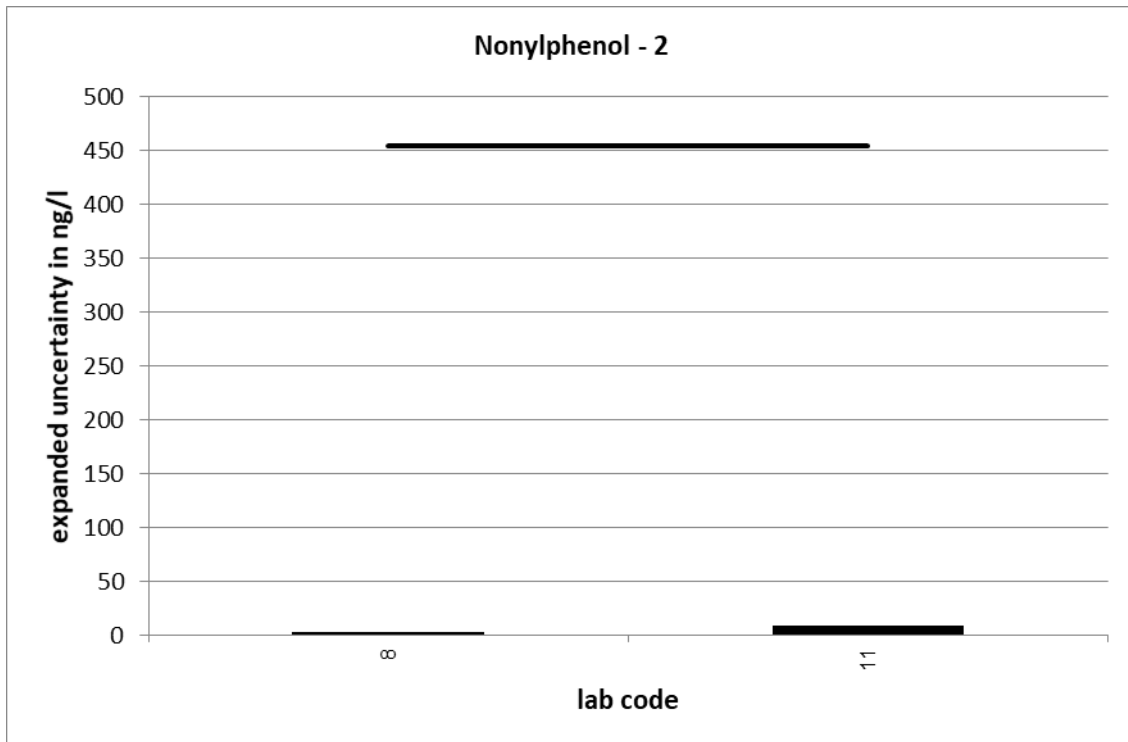
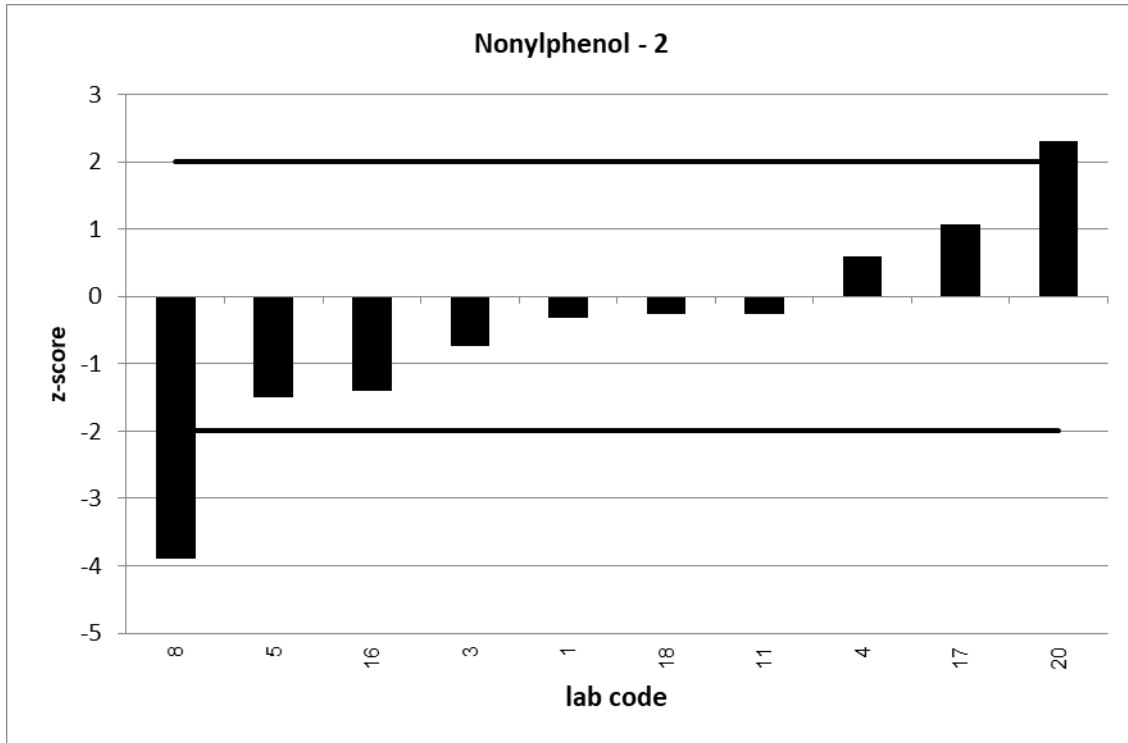


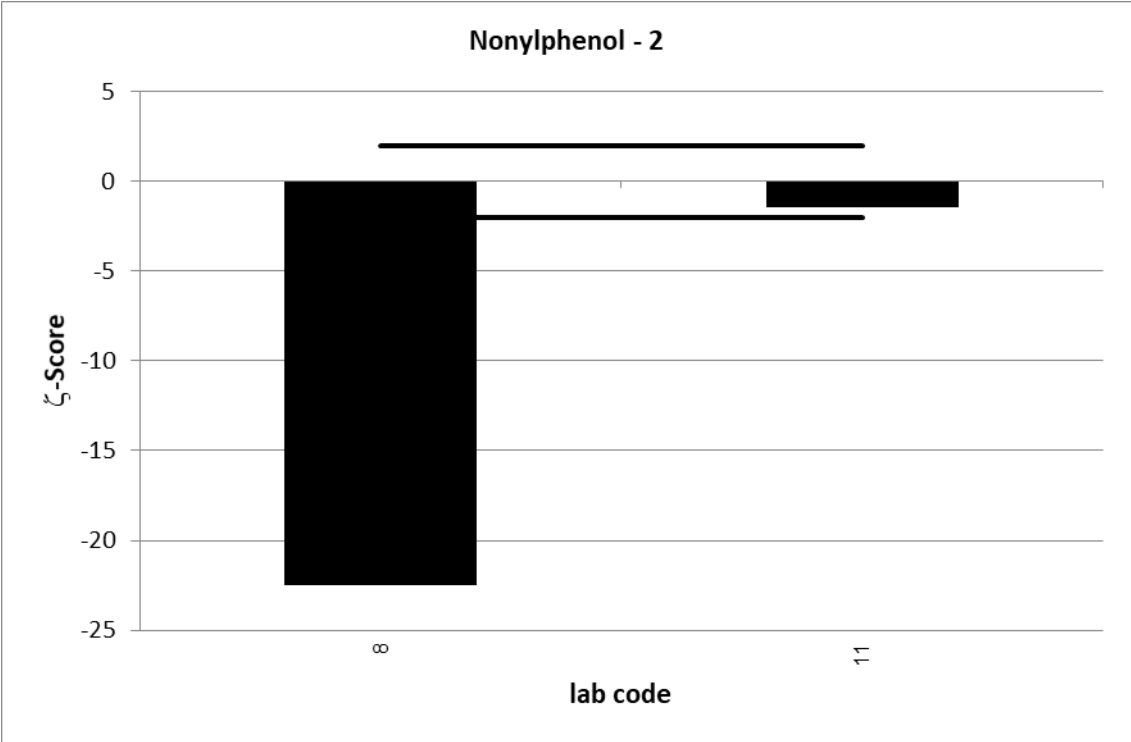
| UKWIR PT 12/21 | | Nonylphenol - 2 | | | |
|------------------------------|---------------|-----------------|---------|---------|------------|
| assigned value [ng/l]* | | 1154 ± 100 | | | |
| upper tolerance limit [ng/l] | | 1731 | | | |
| lower tolerance limit [ng/l] | | 576,9 | | | |
| lab code | result [ng/l] | ± | ζ-score | z-score | assessm.** |
| 1 | 1060 | | | -0,3 | s |
| 3 | 940 | | | -0,7 | s |
| 4 | 1323,75 | | | 0,6 | s |
| 5 | 721 | | | -1,5 | s |
| 8 | 30,99 | 3,1 | -22,5 | -3,9 | u |
| 11 | 1080 | 10 | -1,5 | -0,3 | s |
| 16 | 750 | | | -1,4 | s |
| 17 | 1460 | | | 1,1 | s |
| 18 | 1077 | | | -0,3 | s |
| 20 | 1820 | | | 2,3 | 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



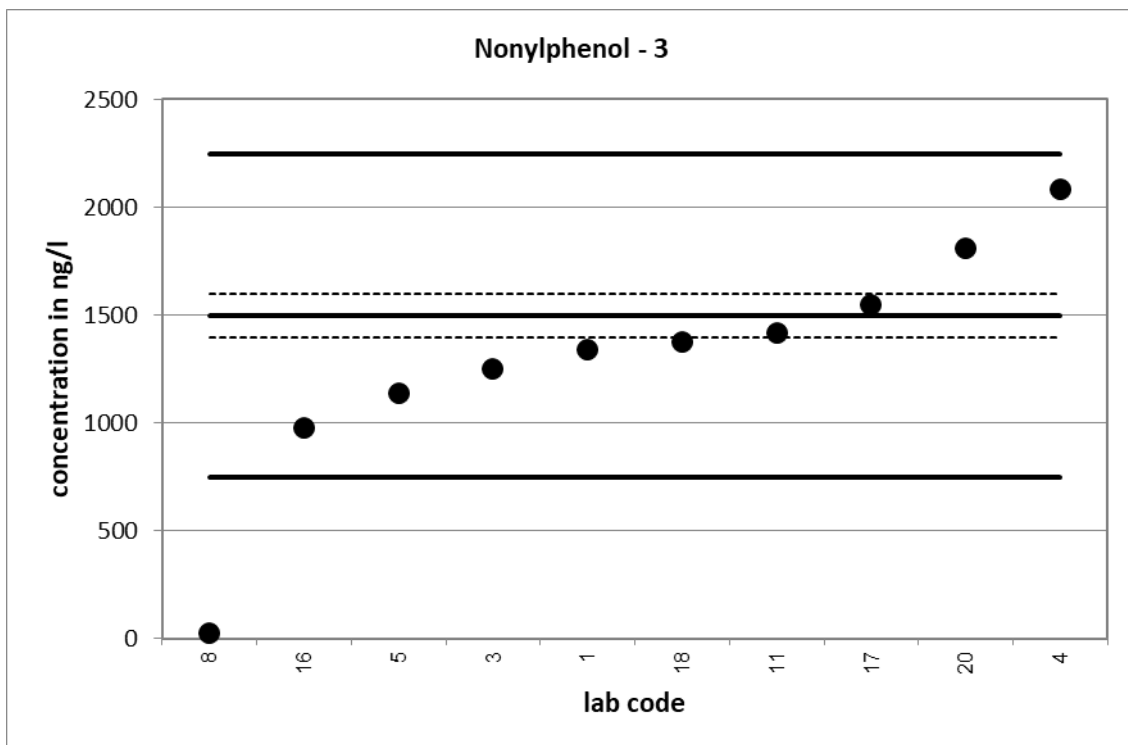


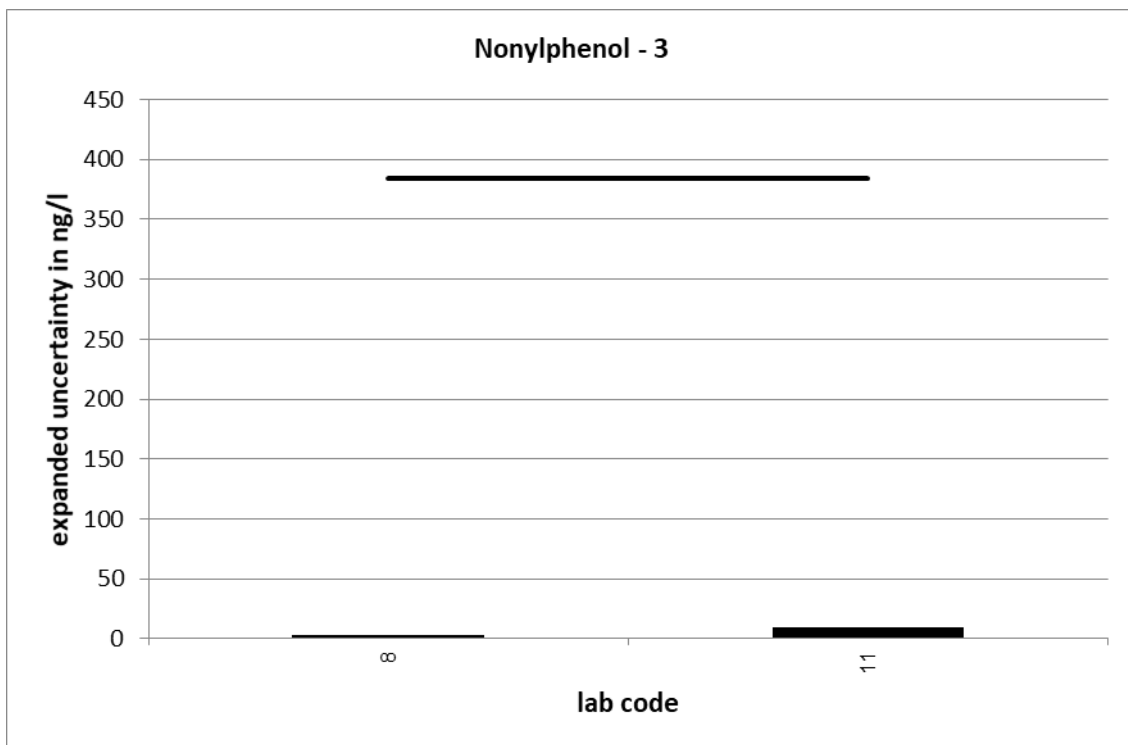
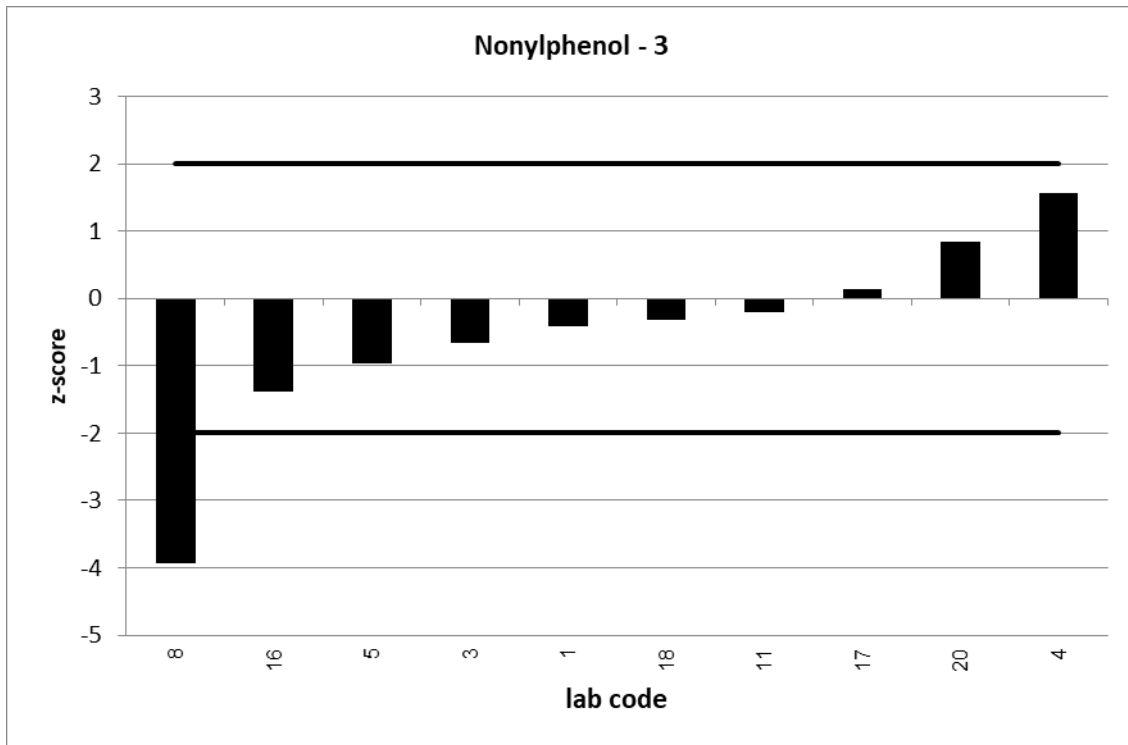


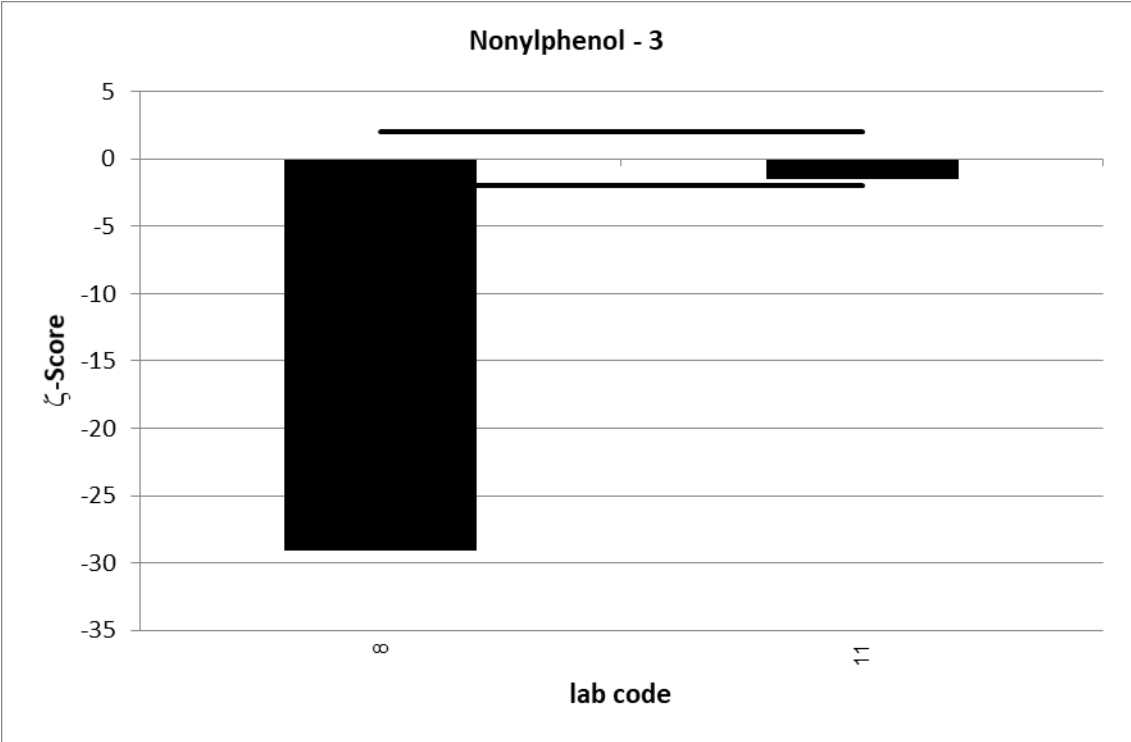
| UKWIR PT 12/21 | | Nonylphenol - 3 | | | |
|------------------------------|---------------|-----------------|---------|---------|------------|
| assigned value [ng/l]* | | 1497 ± 101 | | | |
| upper tolerance limit [ng/l] | | 2245 | | | |
| lower tolerance limit [ng/l] | | 748,3 | | | |
| lab code | result [ng/l] | ± | ζ-score | z-score | assessm.** |
| 1 | 1340 | | | -0,4 | s |
| 3 | 1250 | | | -0,7 | s |
| 4 | 2081,75 | | | 1,6 | s |
| 5 | 1138 | | | -1,0 | s |
| 8 | 28,11 | 3 | -29,1 | -3,9 | u |
| 11 | 1420 | 10 | -1,5 | -0,2 | s |
| 16 | 980 | | | -1,4 | s |
| 17 | 1550 | | | 0,1 | s |
| 18 | 1374 | | | -0,3 | s |
| 20 | 1810 | | | 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

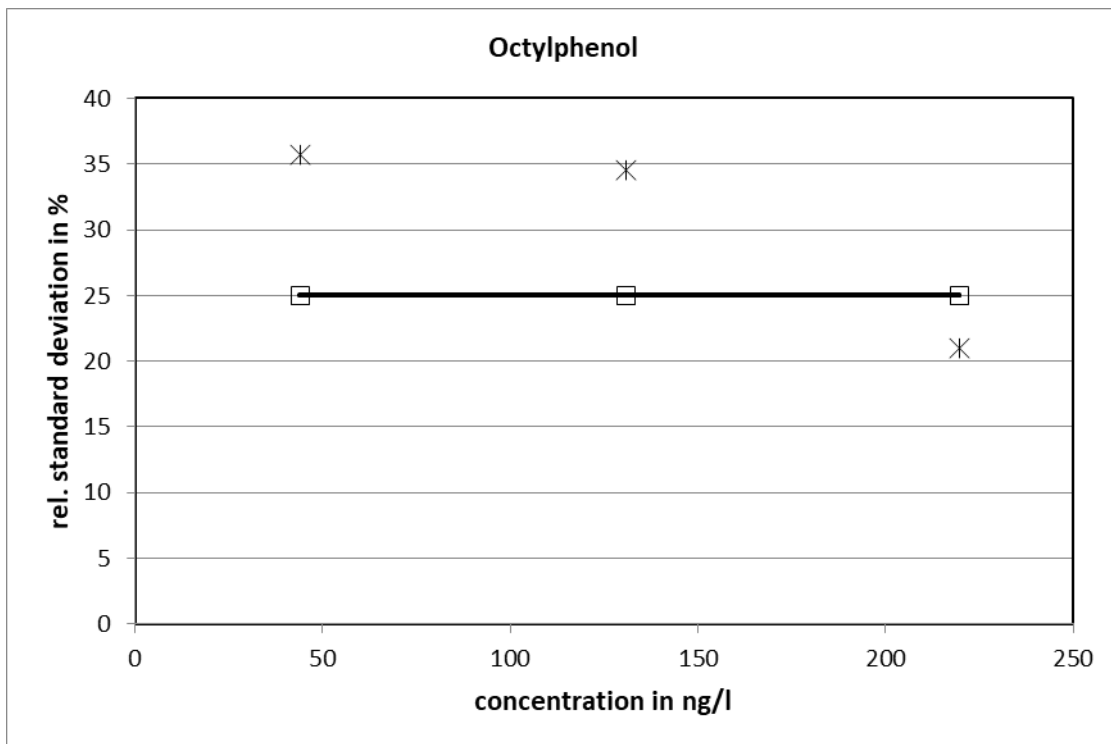






Octylphenol

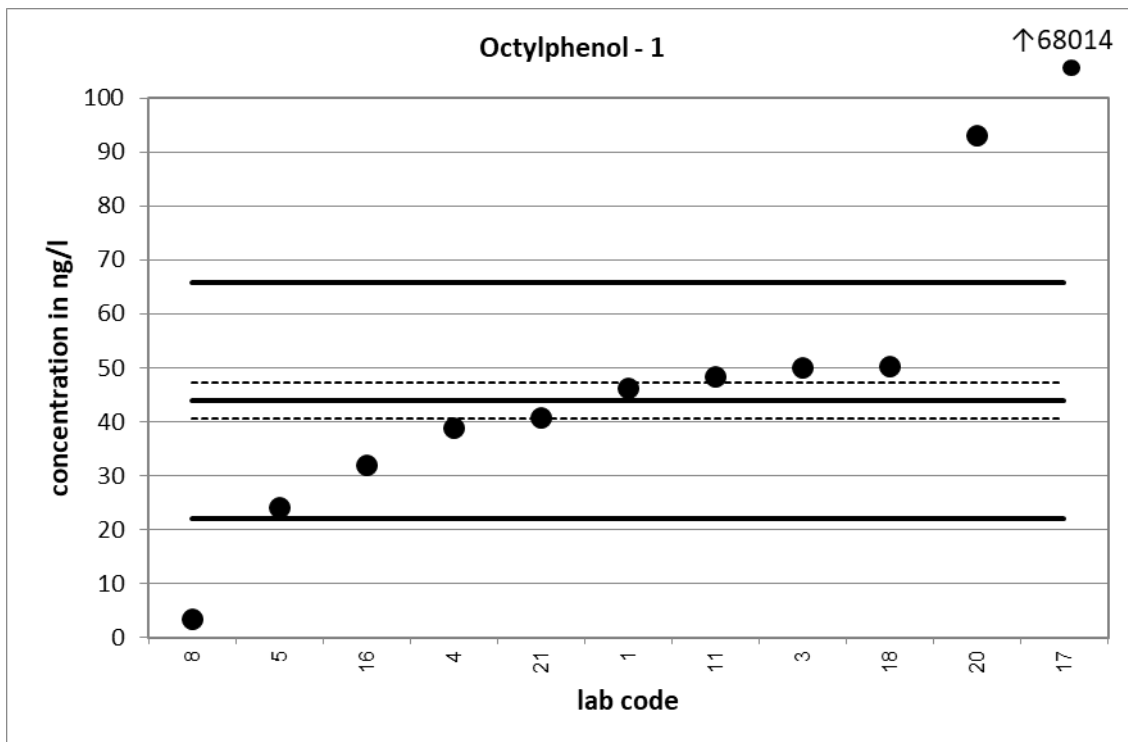
| level | assigned value [ng/l] | expanded uncertainty of the assigned value [%] | standard deviation, calculated using robust statistics [ng/l] | standard deviation for proficiency assessment [ng/l] | standard deviation for proficiency assessment [%] | upper tolerance limit [ng/l] | lower tolerance limit [ng/l] | upper tolerance limit [%] | lower tolerance limit [%] | number of results | out below | out above | out [%] |
|-------|-----------------------|--|---|--|---|------------------------------|------------------------------|---------------------------|---------------------------|-------------------|-----------|-----------|---------|
| 1 | 43,85 | 7,59 | 15,64 | 10,96 | 25 | 65,78 | 21,93 | 50 | -50 | 9 | 1 | 2 | 27,3 |
| 2 | 131,0 | 3,07 | 45,19 | 32,75 | 25 | 196,5 | 65,50 | 50 | -50 | 10 | 1 | 0 | 9,1 |
| 3 | 219,7 | 2,40 | 46,08 | 54,92 | 25 | 329,5 | 109,8 | 50 | -50 | 10 | 2 | 0 | 18,2 |
| | | | | | | | | | sum | 29 | 4 | 2 | 20,7 |

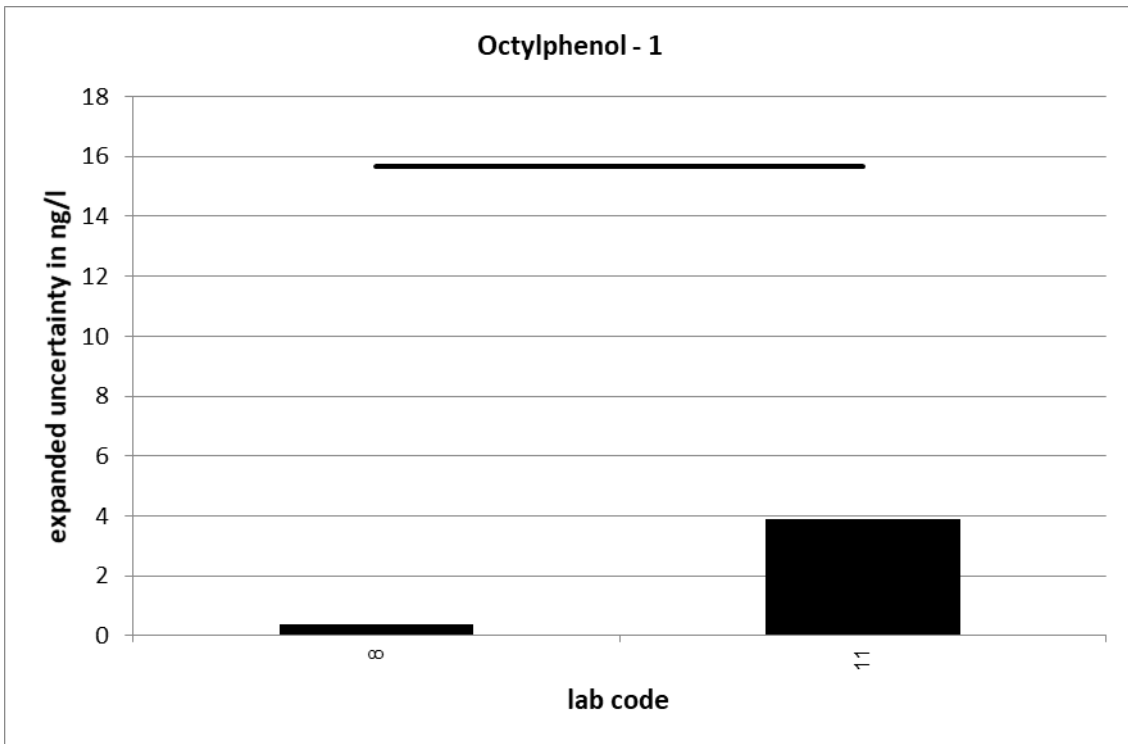
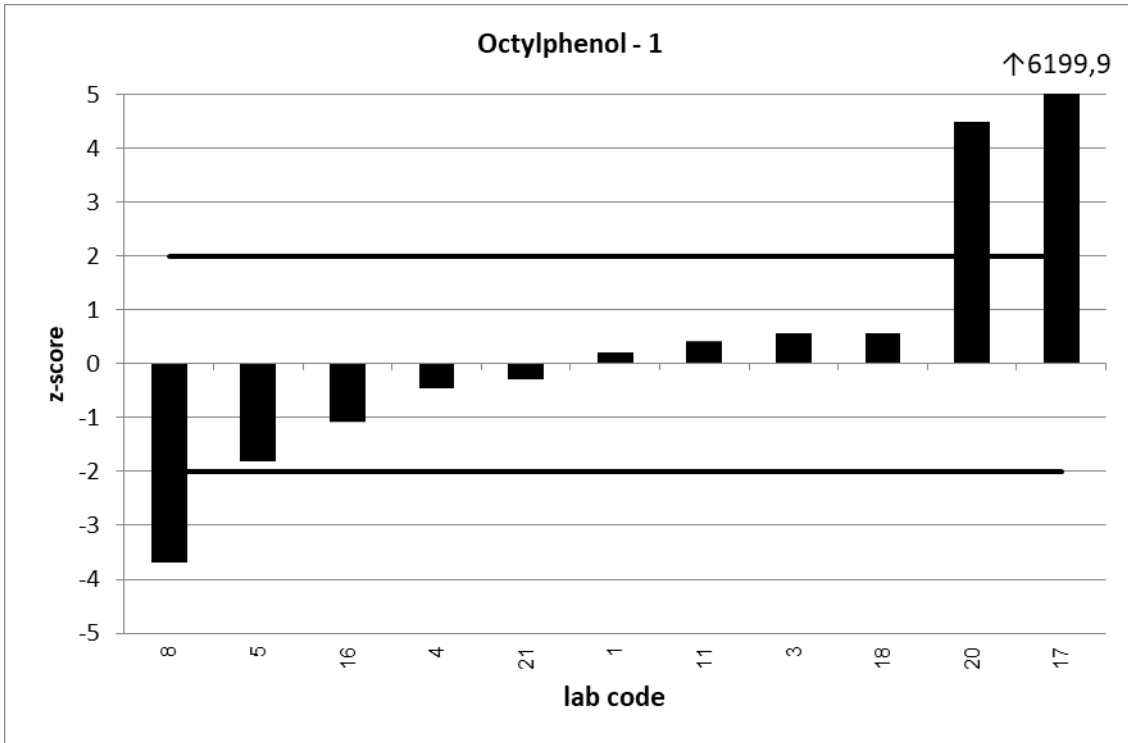


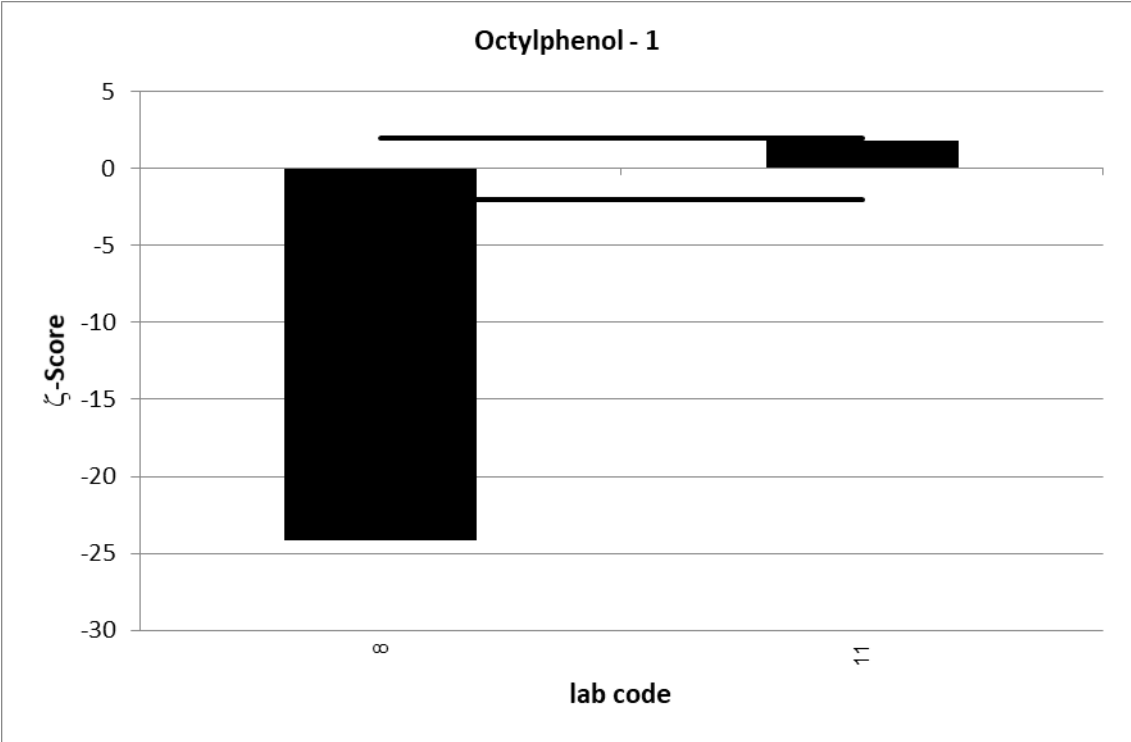
| UKWIR PT 12/21 | | Octylphenol - 1 | | | |
|------------------------------|---------------|-----------------|---------|---------|------------|
| assigned value [ng/l]* | | 43,85 ± 3,33 | | | |
| upper tolerance limit [ng/l] | | 65,78 | | | |
| lower tolerance limit [ng/l] | | 21,93 | | | |
| lab code | result [ng/l] | ± | ζ-score | z-score | assessm.** |
| 1 | 46,1 | | | 0,2 | s |
| 3 | 50 | | | 0,6 | s |
| 4 | 38,85 | | | -0,5 | s |
| 5 | 24 | | | -1,8 | s |
| 8 | 3,35 | 0,4 | -24,2 | -3,7 | u |
| 11 | 48,4 | 3,9 | 1,8 | 0,4 | s |
| 16 | 32 | | | -1,1 | s |
| 17 | 68014 | | | 6199,9 | u |
| 18 | 50,1 | | | 0,6 | s |
| 20 | 93,1 | | | 4,5 | u |
| 21 | 40,6 | | | -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



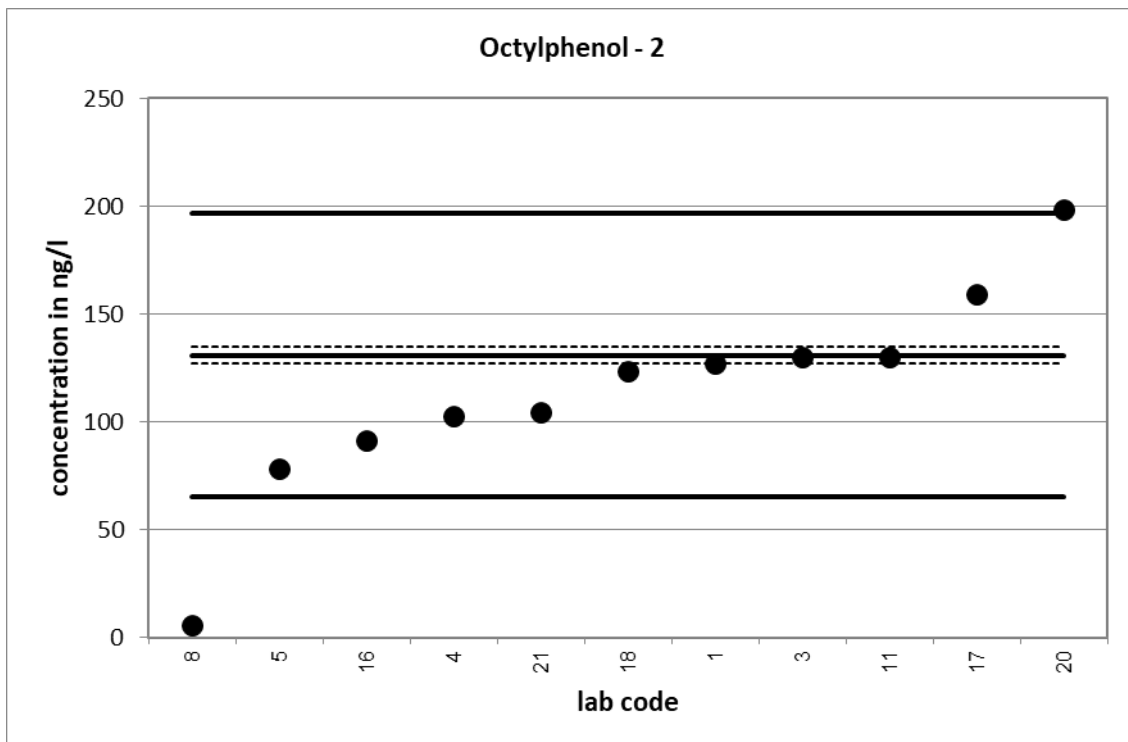


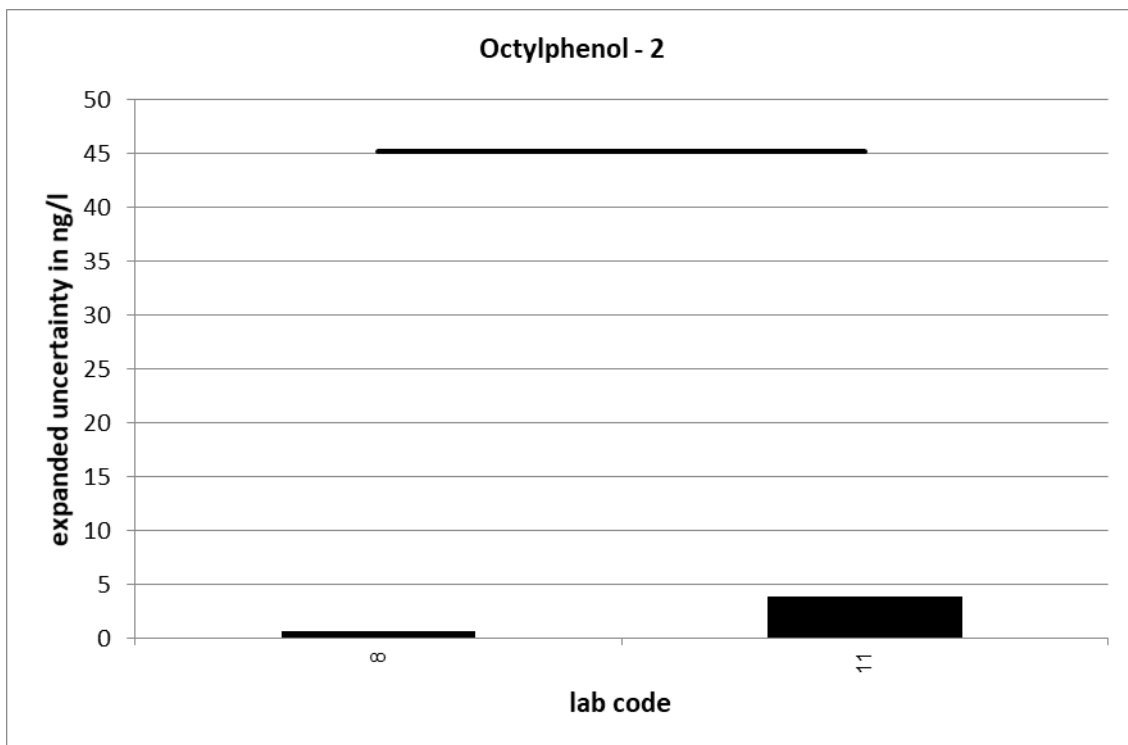
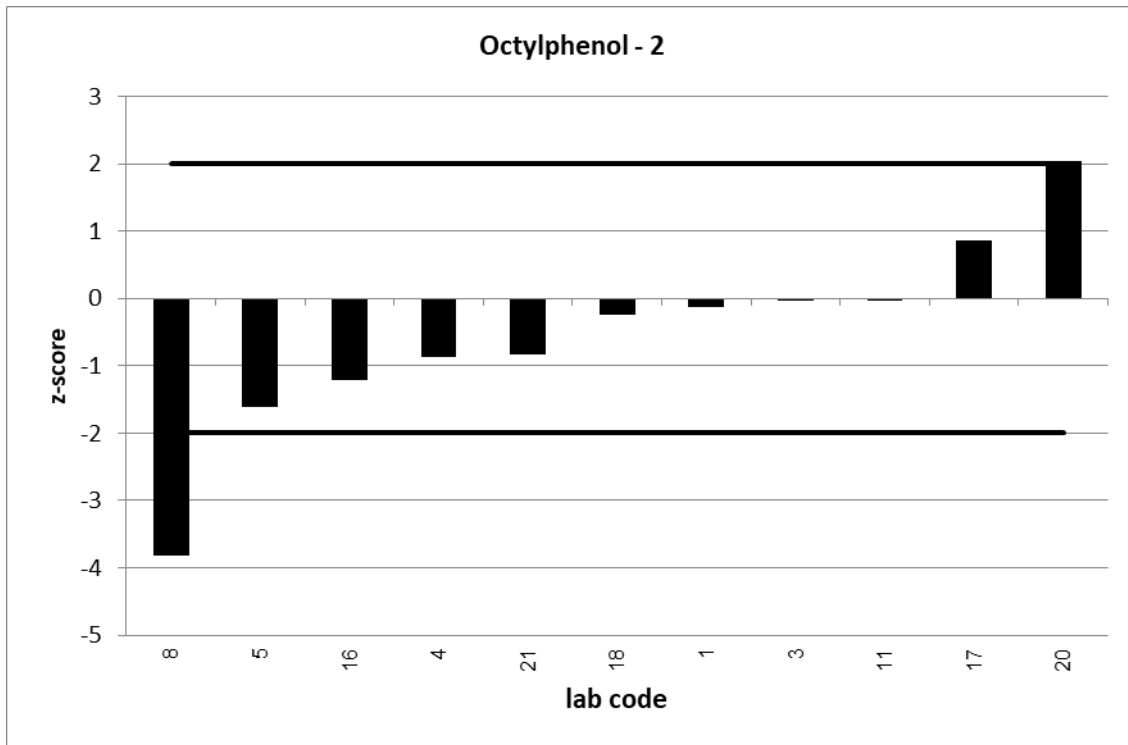


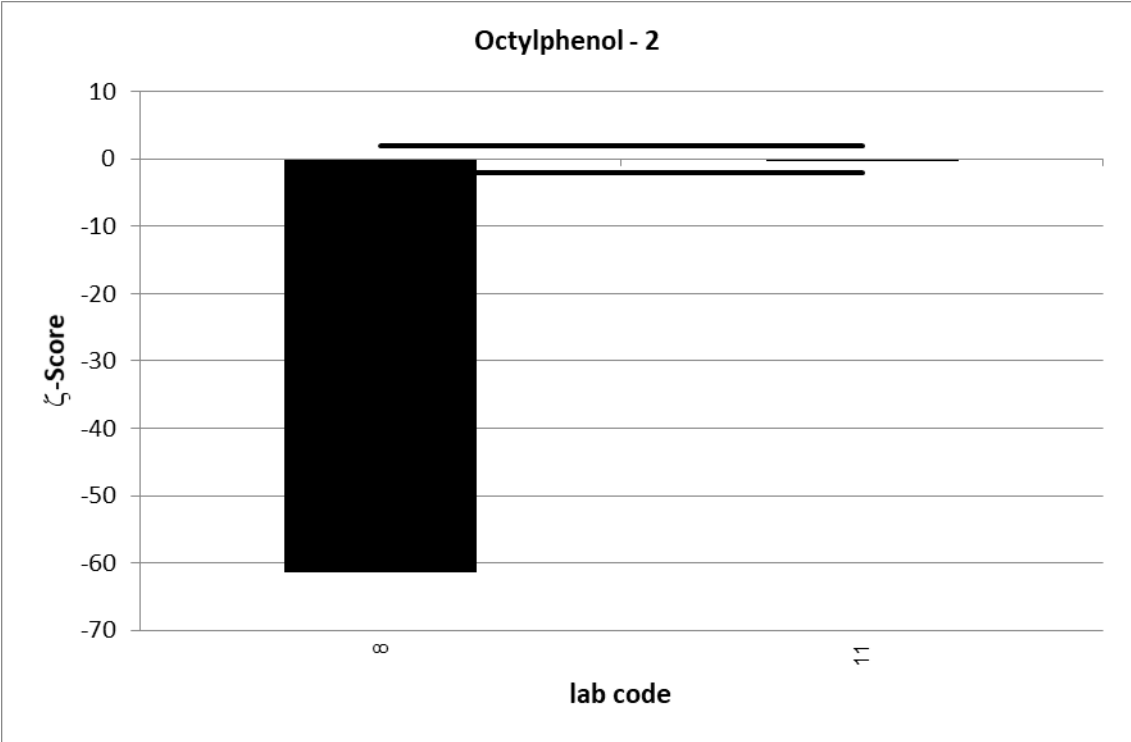
| UKWIR PT 12/21 | | Octylphenol - 2 | | | |
|------------------------------|---------------|-----------------|---------|---------|------------|
| assigned value [ng/l]* | | 131 ± 4 | | | |
| upper tolerance limit [ng/l] | | 196,5 | | | |
| lower tolerance limit [ng/l] | | 65,5 | | | |
| lab code | result [ng/l] | ± | ζ-score | z-score | assessm.** |
| 1 | 127 | | | -0,1 | s |
| 3 | 130 | | | 0,0 | s |
| 4 | 102,45 | | | -0,9 | s |
| 5 | 78 | | | -1,6 | s |
| 8 | 5,7 | 0,68 | -61,5 | -3,8 | u |
| 11 | 130 | 3,9 | -0,4 | 0,0 | s |
| 16 | 91 | | | -1,2 | s |
| 17 | 159 | | | 0,9 | s |
| 18 | 123 | | | -0,2 | s |
| 20 | 198 | | | 2,0 | s |
| 21 | 104 | | | -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



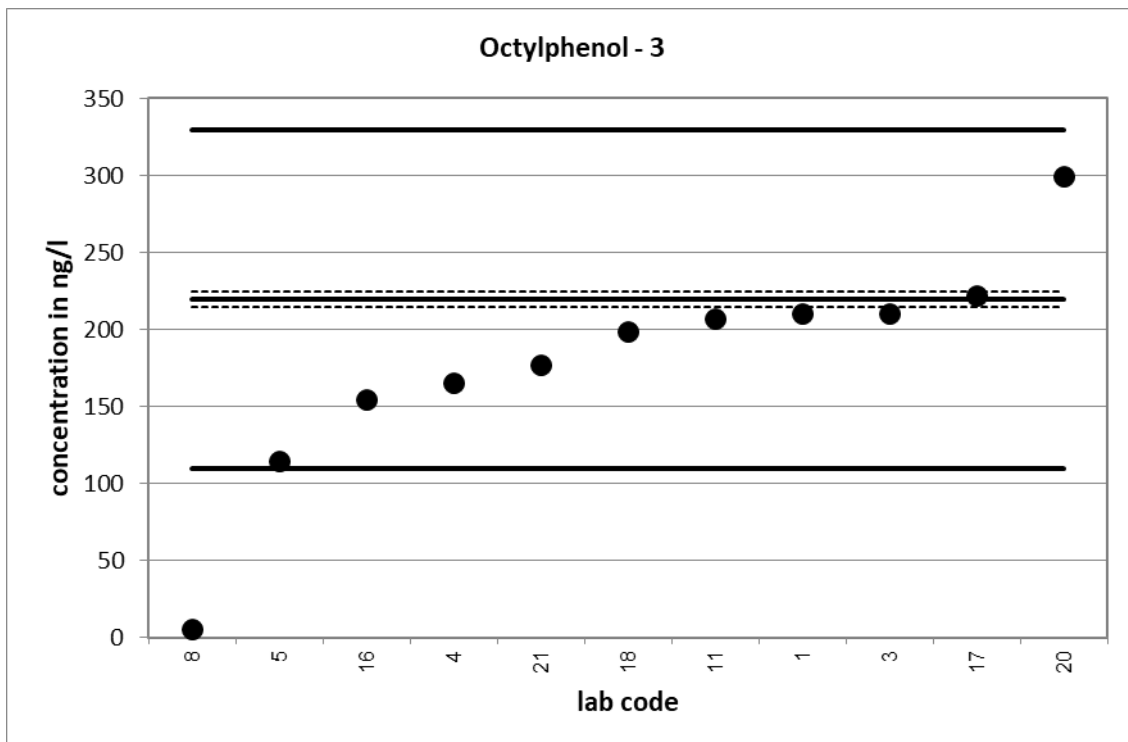


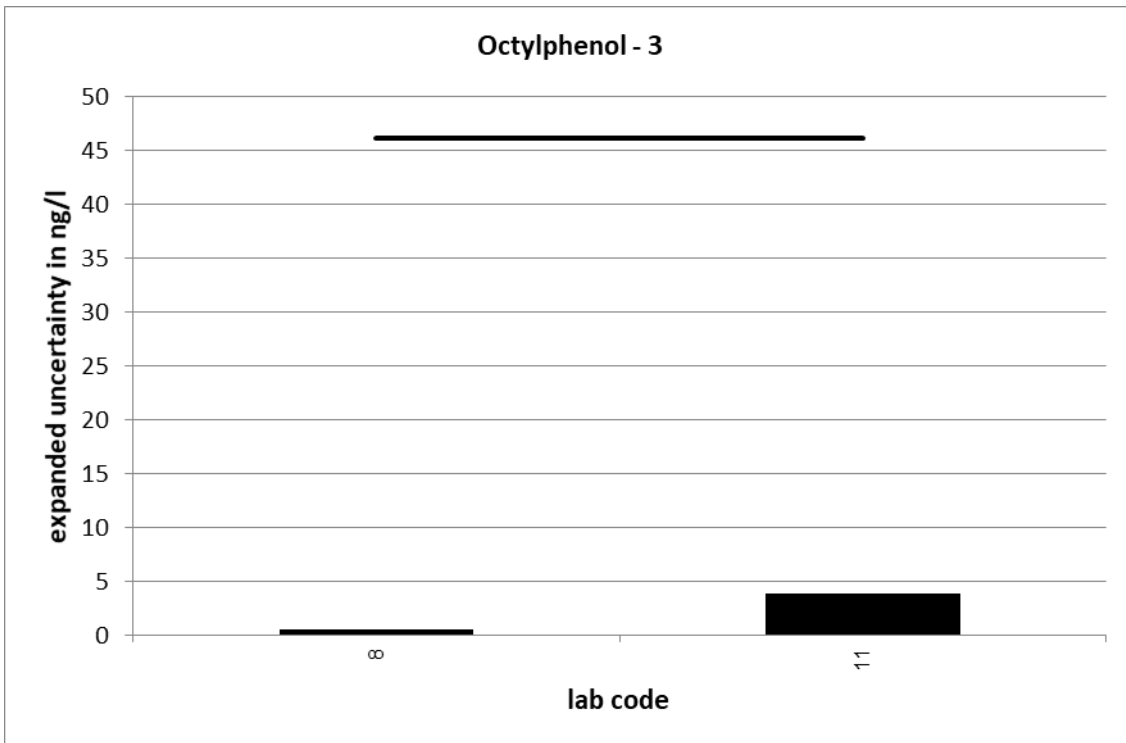
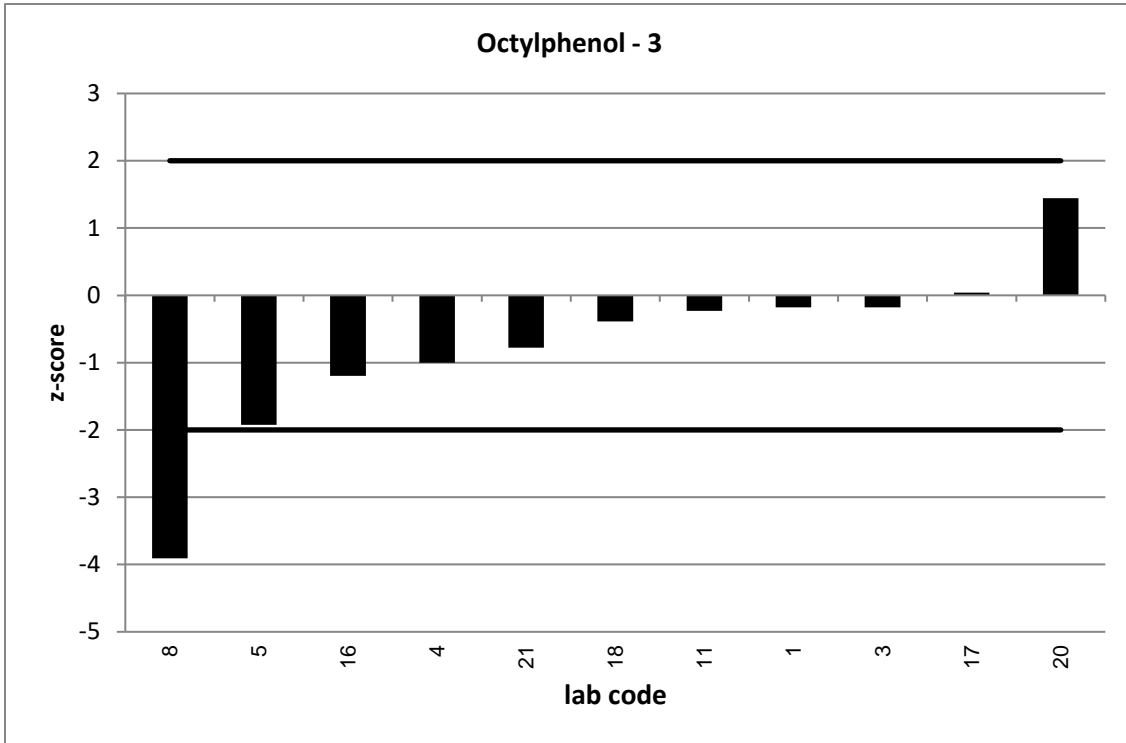


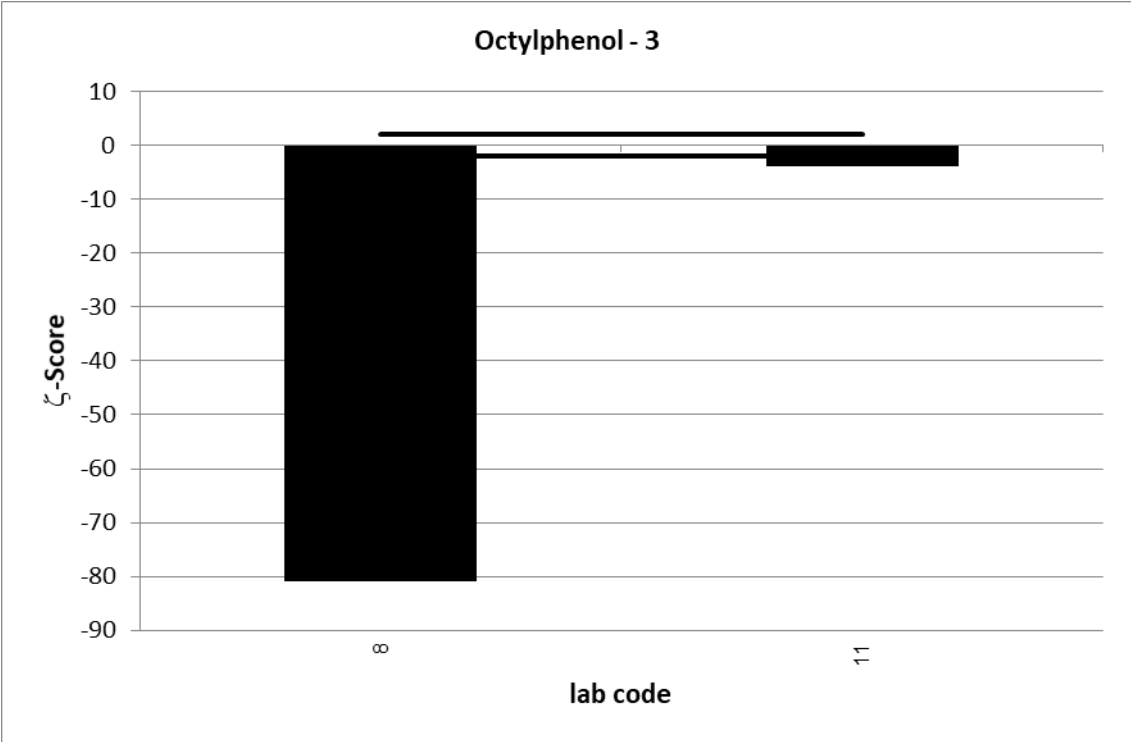
| UKWIR PT 12/21 | | Octylphenol - 3 | | | |
|------------------------------|---------------|-----------------|---------|---------|------------|
| assigned value [ng/l]* | | 219,7 ± 5,3 | | | |
| upper tolerance limit [ng/l] | | 329,5 | | | |
| lower tolerance limit [ng/l] | | 109,8 | | | |
| lab code | result [ng/l] | ± | ζ-score | z-score | assessm.** |
| 1 | 210 | | | -0,2 | s |
| 3 | 210 | | | -0,2 | s |
| 4 | 164,75 | | | -1,0 | s |
| 5 | 114 | | | -1,9 | s |
| 8 | 4,99 | 0,6 | -80,9 | -3,9 | u |
| 11 | 207 | 3,9 | -3,9 | -0,2 | s |
| 16 | 154 | | | -1,2 | s |
| 17 | 222 | | | 0,0 | s |
| 18 | 198,4 | | | -0,4 | s |
| 20 | 299 | | | 1,4 | s |
| 21 | 177 | | | -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



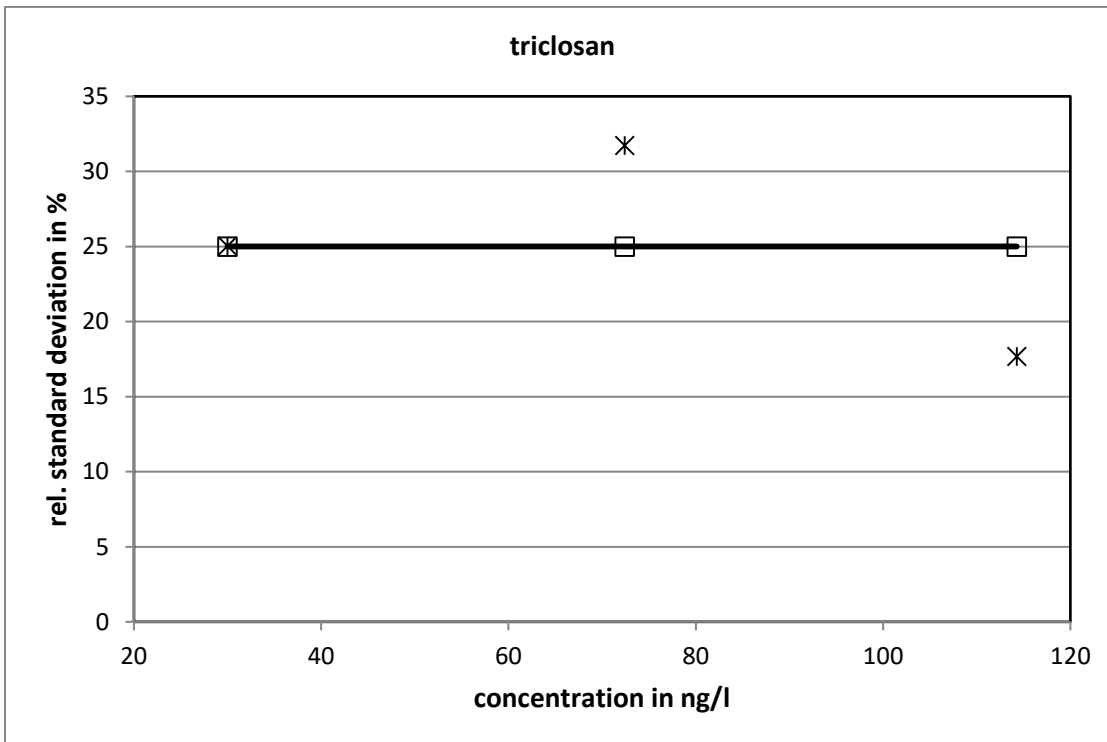




UKWIR 13/21:

| triclosan | | | | | | | | | | | | | |
|-----------|-----------------------|--|---|--|---|------------------------------|------------------------------|---------------------------|---------------------------|-------------------|-----------|-----------|---------|
| 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 | 29,98 | 20,86 | 7,505 | 7,496 | 25 | 44,97 | 14,99 | 50 | -50 | 9 | 0 | 0 | 0,0 |
| 2 | 72,39 | 26,44 | 22,97 | 18,10 | 25 | 108,6 | 36,19 | 50 | -50 | 9 | 0 | 0 | 0,0 |
| 3 | 114,3 | 14,73 | 20,19 | 28,57 | 25 | 171,4 | 57,14 | 50 | -50 | 9 | 0 | 0 | 0,0 |
| | | | | | | | | | | sum | 27 | 0 | 0,0 |

Relative standard deviation

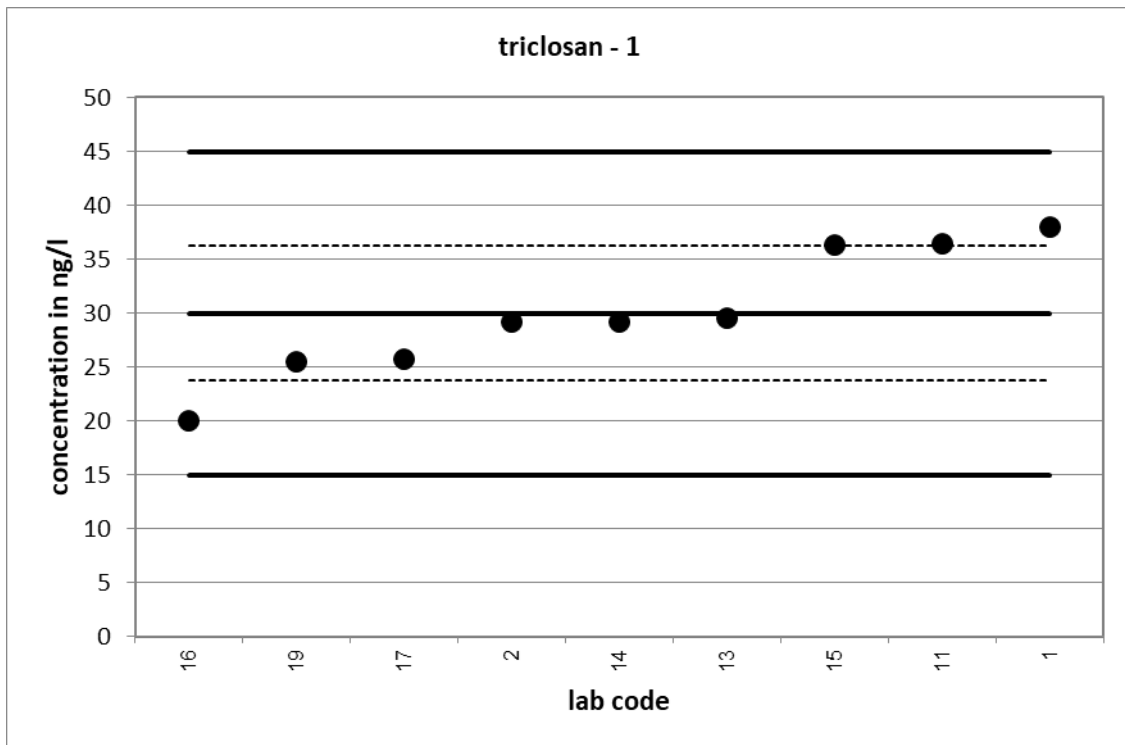


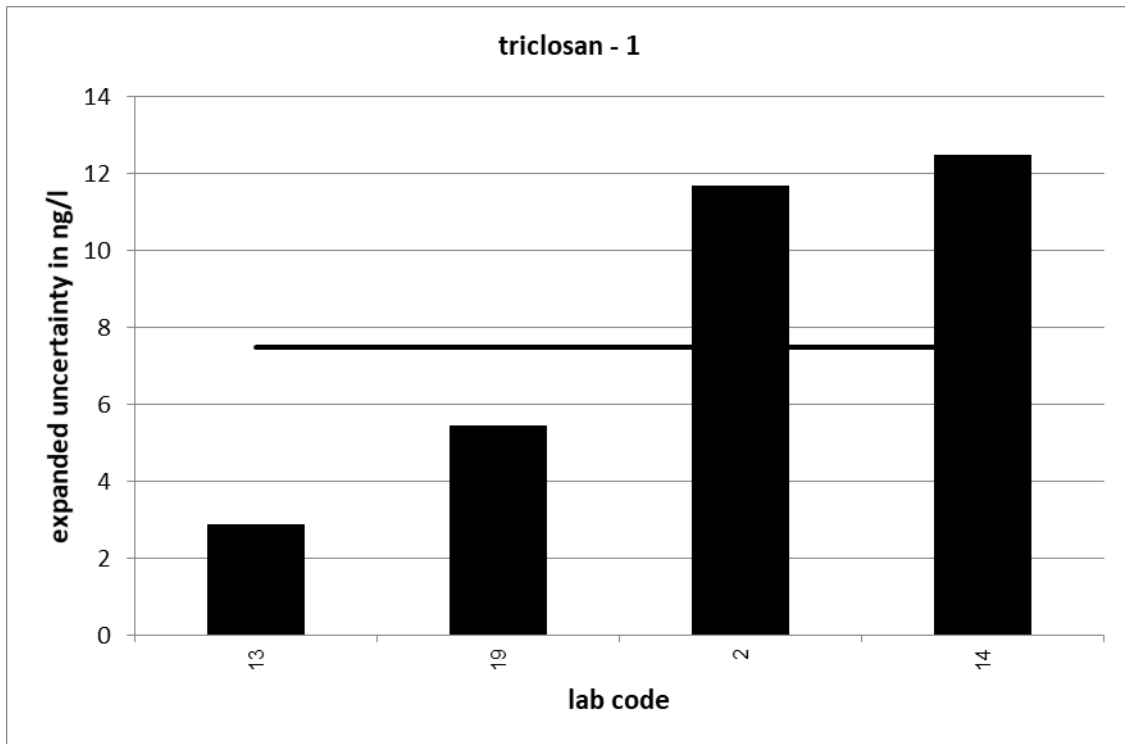
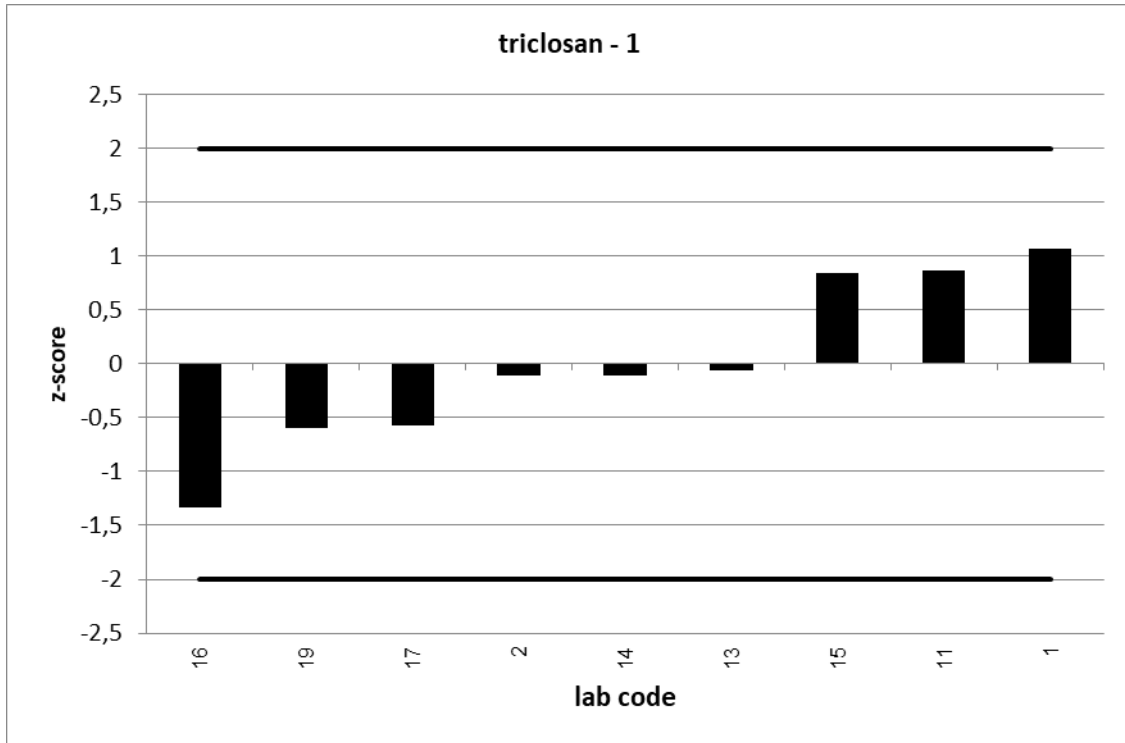
25 % is used as standard deviation for proficiency assessment.

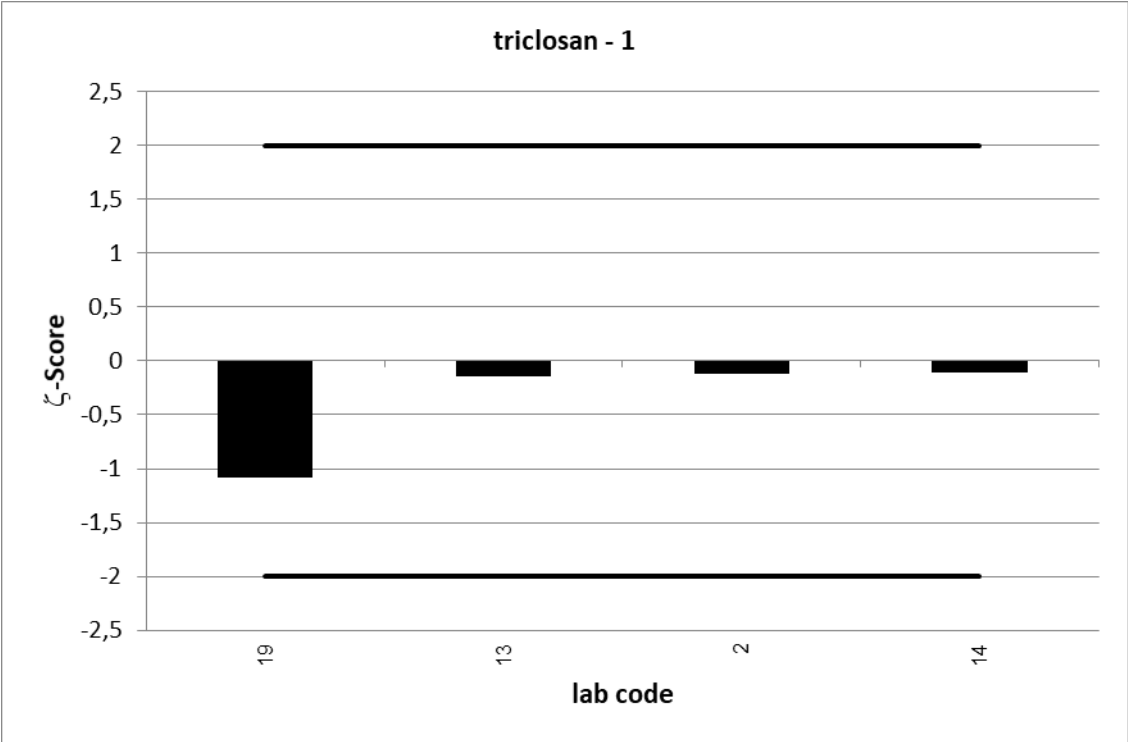
| UKWIR PT 13/21 | | triclosan - 1 | | | |
|------------------------------|---------------|---------------|---------|---------|------------|
| assigned value [ng/l]* | | 29,98 ± 6,25 | | | |
| upper tolerance limit [ng/l] | | 44,97 | | | |
| lower tolerance limit [ng/l] | | 14,99 | | | |
| lab code | result [ng/l] | ± | ζ-score | z-score | assessm.** |
| 1 | 38 | | | 1,1 | s |
| 2 | 29,2 | 11,7 | -0,1 | -0,1 | s |
| 11 | 36,45 | | | 0,9 | s |
| 13 | 29,5 | 2,9 | -0,1 | -0,1 | s |
| 14 | 29,2 | 12,5 | -0,1 | -0,1 | s |
| 15 | 36,3 | | | 0,8 | s |
| 16 | 20 | | | -1,3 | s |
| 17 | 25,7 | | | -0,6 | s |
| 19 | 25,5 | 5,47 | -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



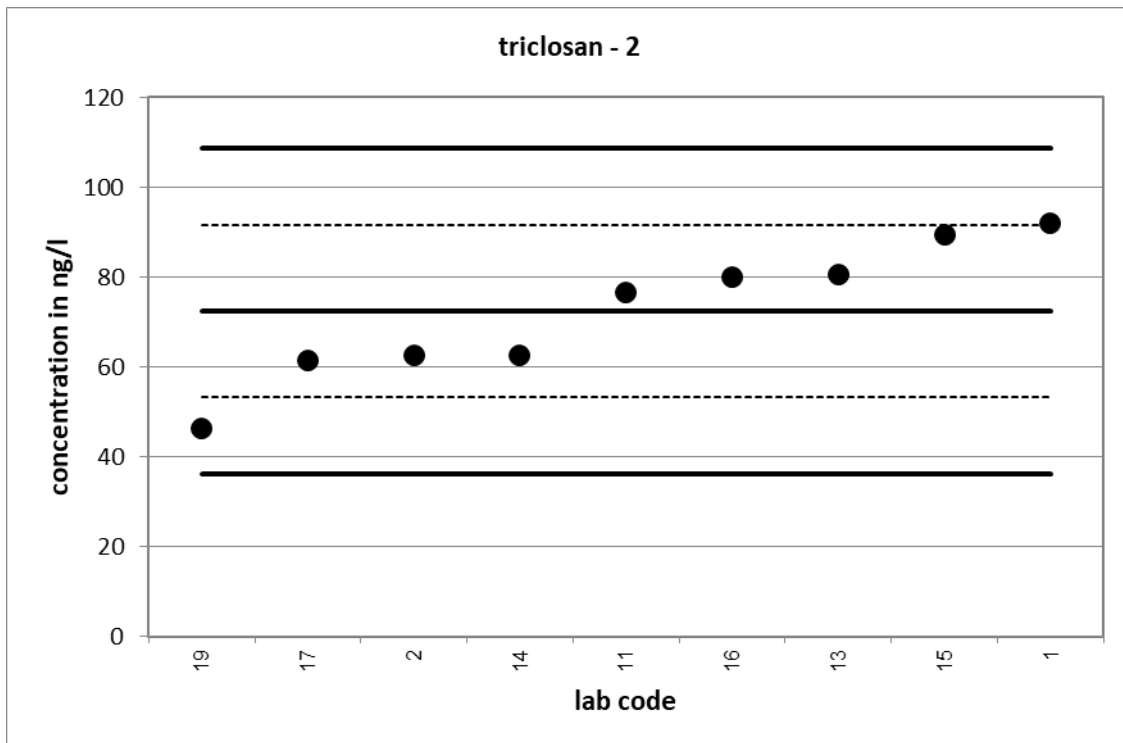


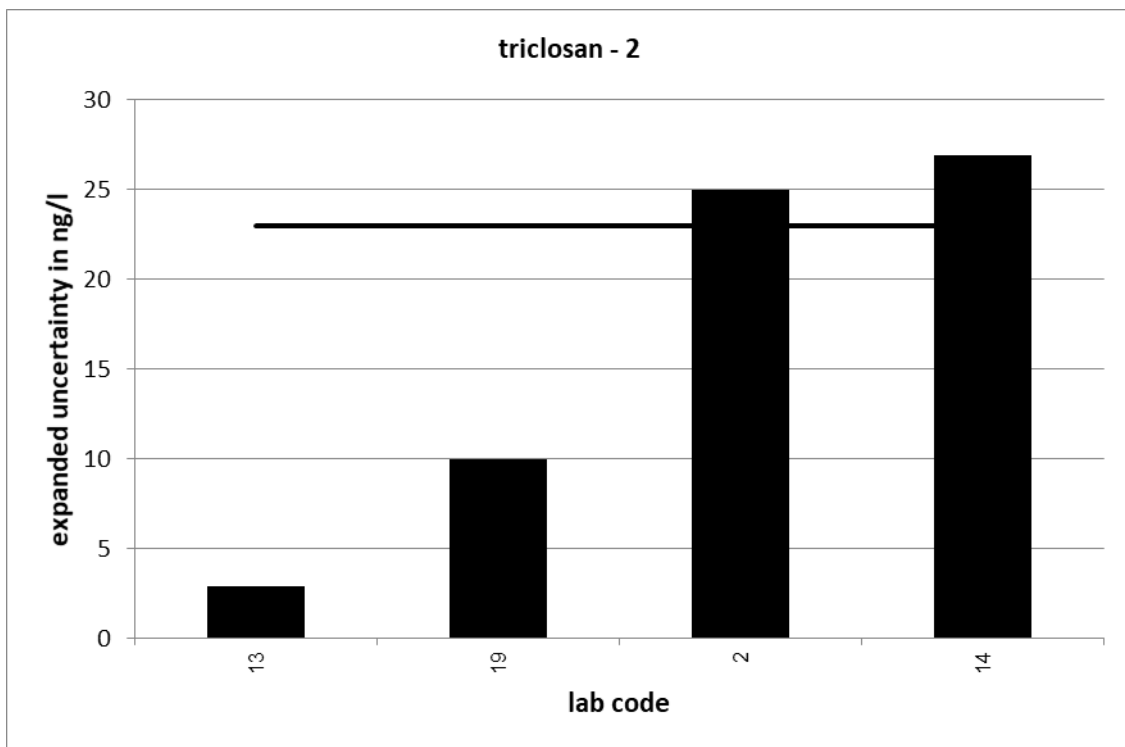
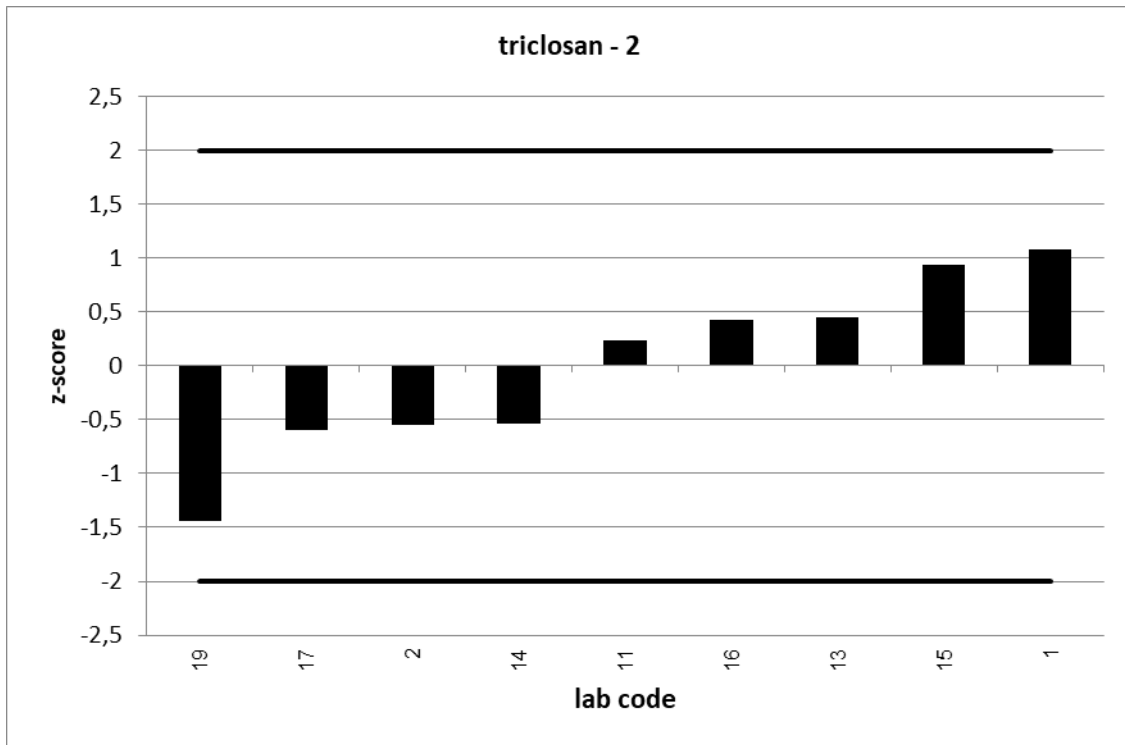


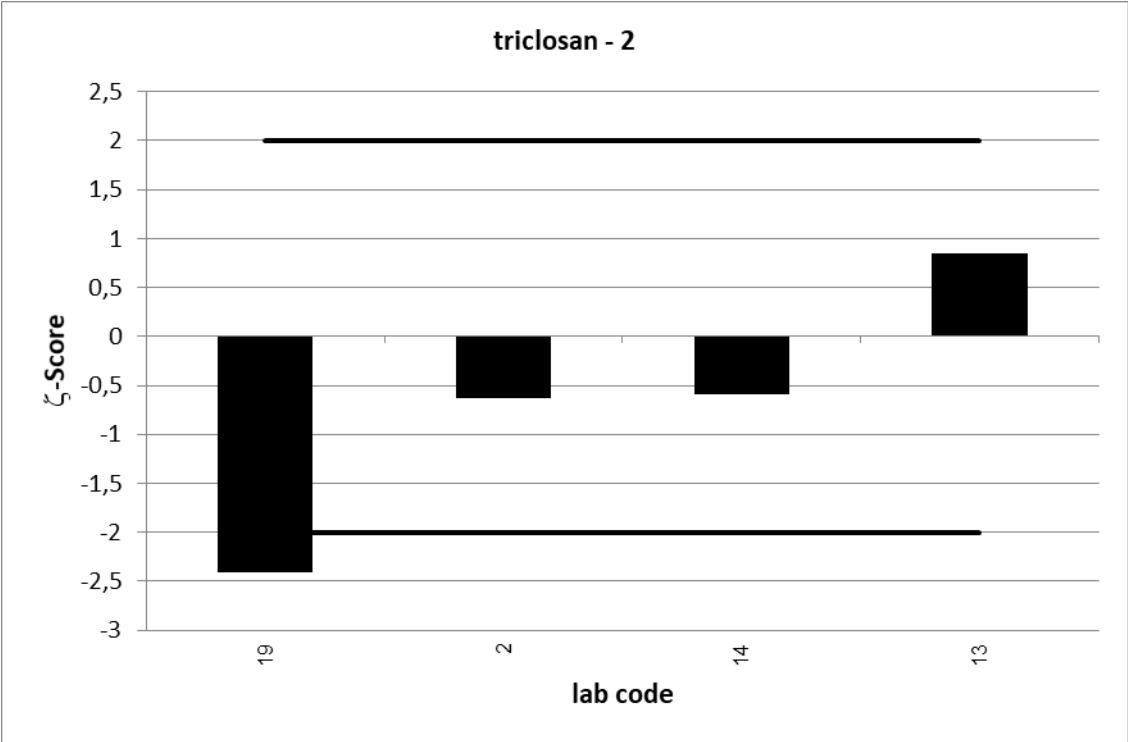
| UKWIR PT 13/21 | | triclosan - 2 | | | |
|------------------------------|---------------|---------------|---------|---------|------------|
| assigned value [ng/l]* | | 72,39 ± 19,14 | | | |
| upper tolerance limit [ng/l] | | 108,6 | | | |
| lower tolerance limit [ng/l] | | 36,19 | | | |
| lab code | result [ng/l] | ± | ζ-score | z-score | assessm.** |
| 1 | 92 | | | 1,1 | s |
| 2 | 62,5 | 25 | -0,6 | -0,5 | s |
| 11 | 76,6 | | | 0,2 | s |
| 13 | 80,6 | 2,9 | 0,8 | 0,5 | s |
| 14 | 62,6 | 26,9 | -0,6 | -0,5 | s |
| 15 | 89,3 | | | 0,9 | s |
| 16 | 80 | | | 0,4 | s |
| 17 | 61,5 | | | -0,6 | s |
| 19 | 46,4 | 9,98 | -2,4 | -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



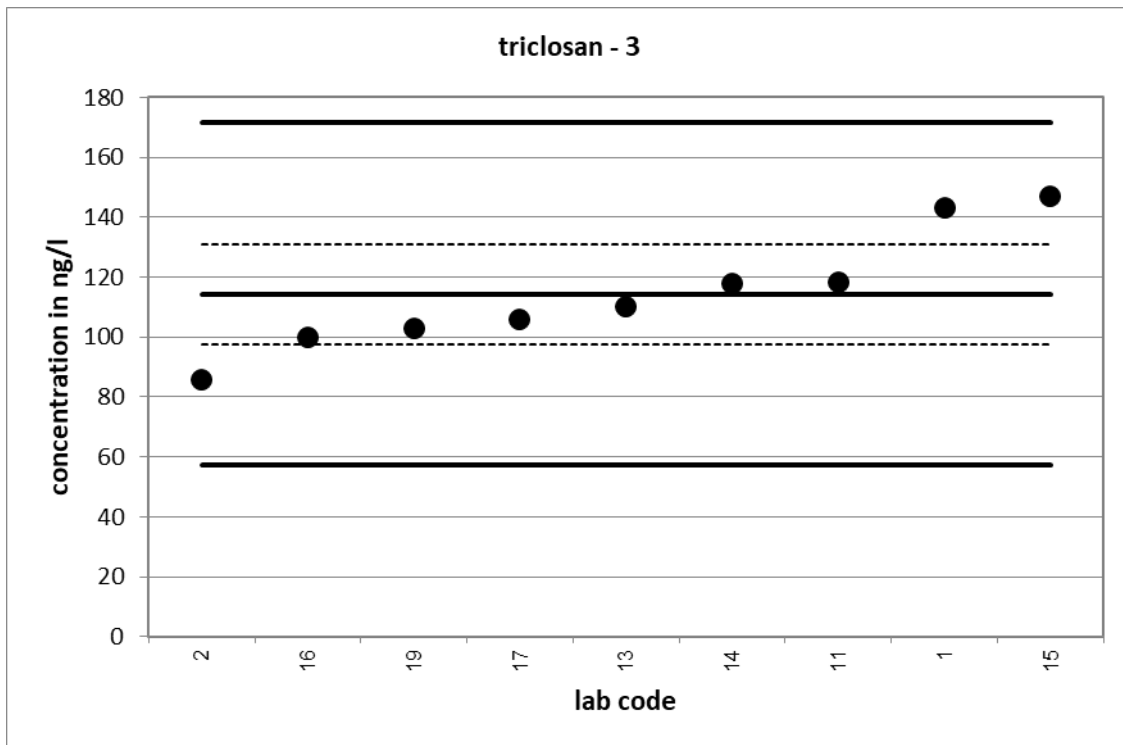


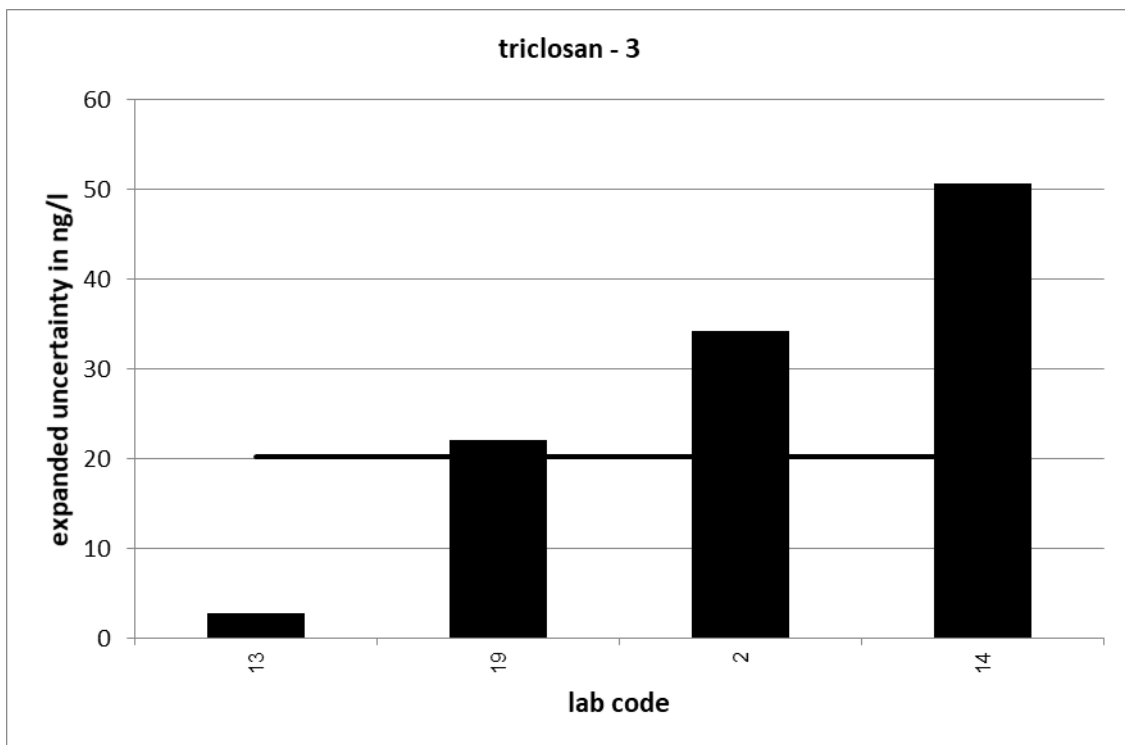
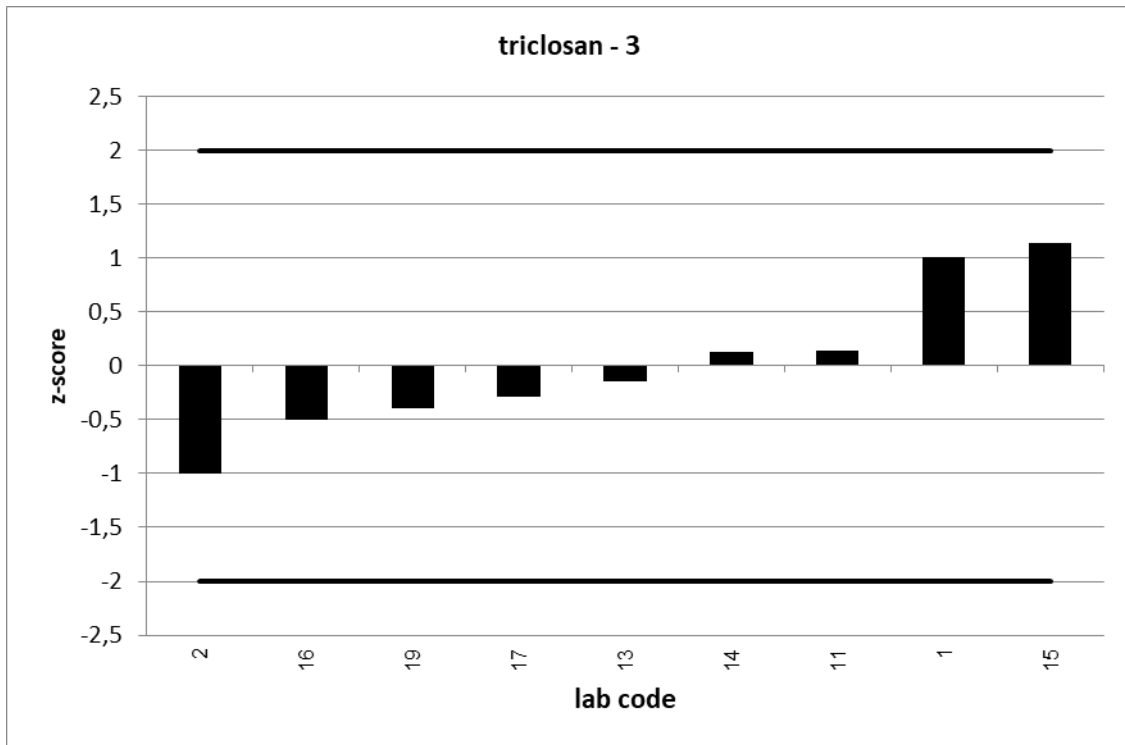


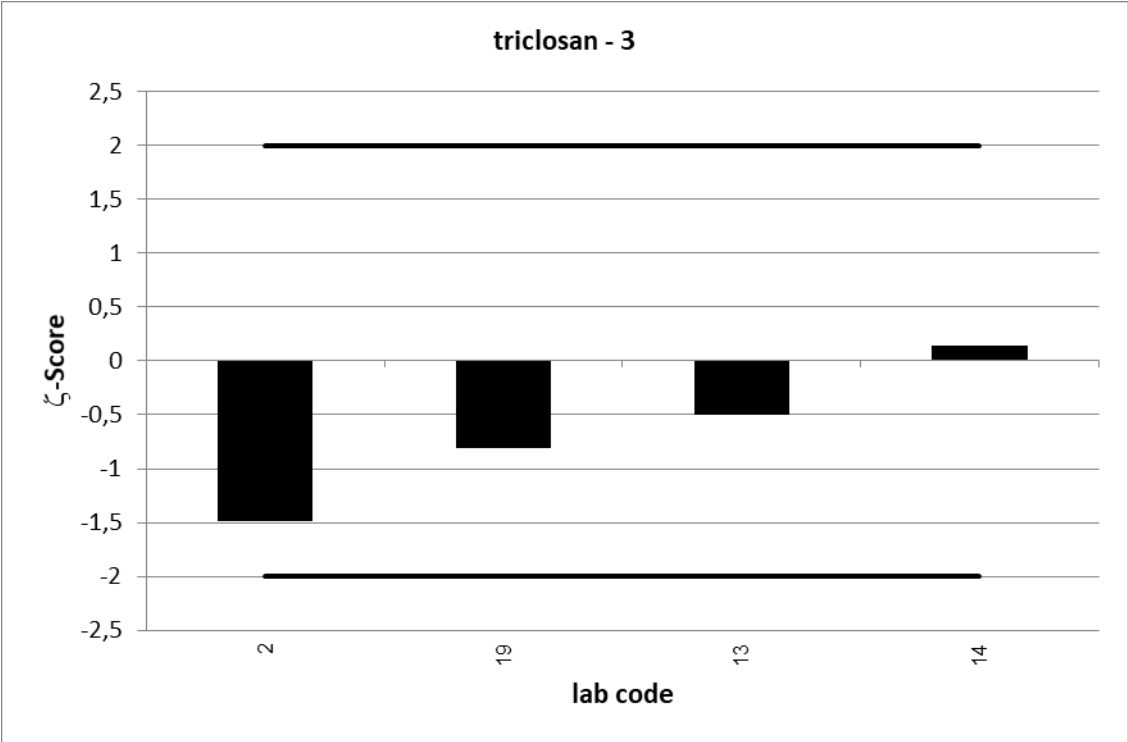
| UKWIR PT 13/21 | | triclosan - 3 | | | |
|------------------------------|---------------|---------------|---------|---------|------------|
| assigned value [ng/l]* | | 114,3 ± 16,8 | | | |
| upper tolerance limit [ng/l] | | 171,4 | | | |
| lower tolerance limit [ng/l] | | 57,14 | | | |
| lab code | result [ng/l] | ± | ζ-score | z-score | assessm.** |
| 1 | 143 | | | 1,0 | s |
| 2 | 85,8 | 34,3 | -1,5 | -1,0 | s |
| 11 | 118,2 | | | 0,1 | s |
| 13 | 110 | 2,9 | -0,5 | -0,1 | s |
| 14 | 118 | 50,7 | 0,1 | 0,1 | s |
| 15 | 147 | | | 1,1 | s |
| 16 | 100 | | | -0,5 | s |
| 17 | 105,9 | | | -0,3 | s |
| 19 | 103 | 22,1 | -0,8 | -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



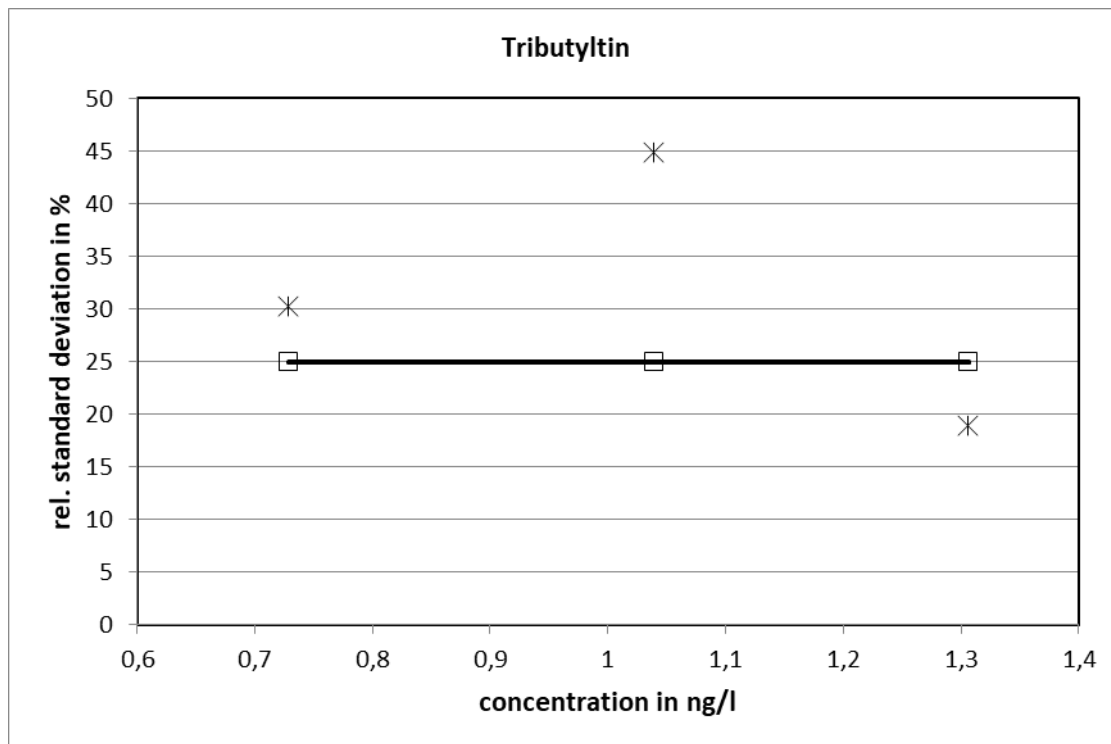




UKWIR 14/21:

| 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 | 0,7287 | 30,91 | 0,2207 | 0,1822 | 25 | 1,093 | 0,3644 | 50 | -50 | 6 | 0 | 0 | 0,0 |
| 2 | 1,039 | 45,79 | 0,4660 | 0,2597 | 25 | 1,558 | 0,5193 | 50 | -50 | 6 | 0 | 0 | 0,0 |
| 3 | 1,306 | 19,31 | 0,2471 | 0,3266 | 25 | 1,960 | 0,6532 | 50 | -50 | 6 | 0 | 0 | 0,0 |
| | | | | | | | | | | sum | 18 | 0 | 0,0 |

Relative standard deviation

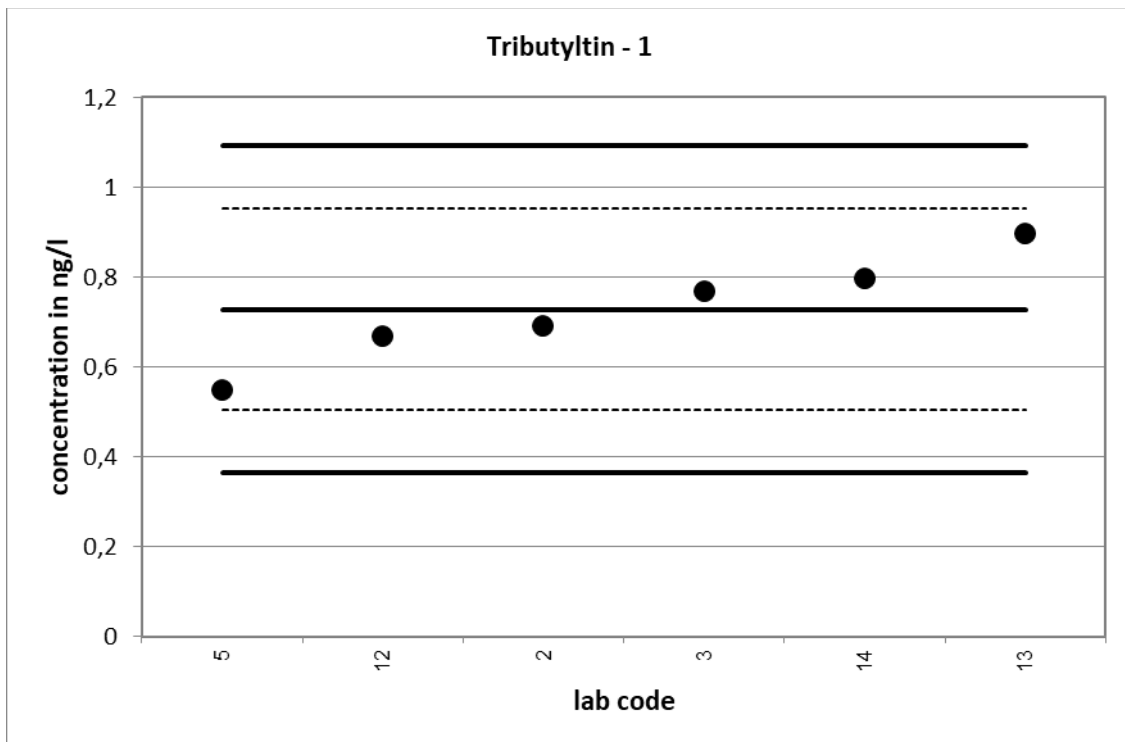


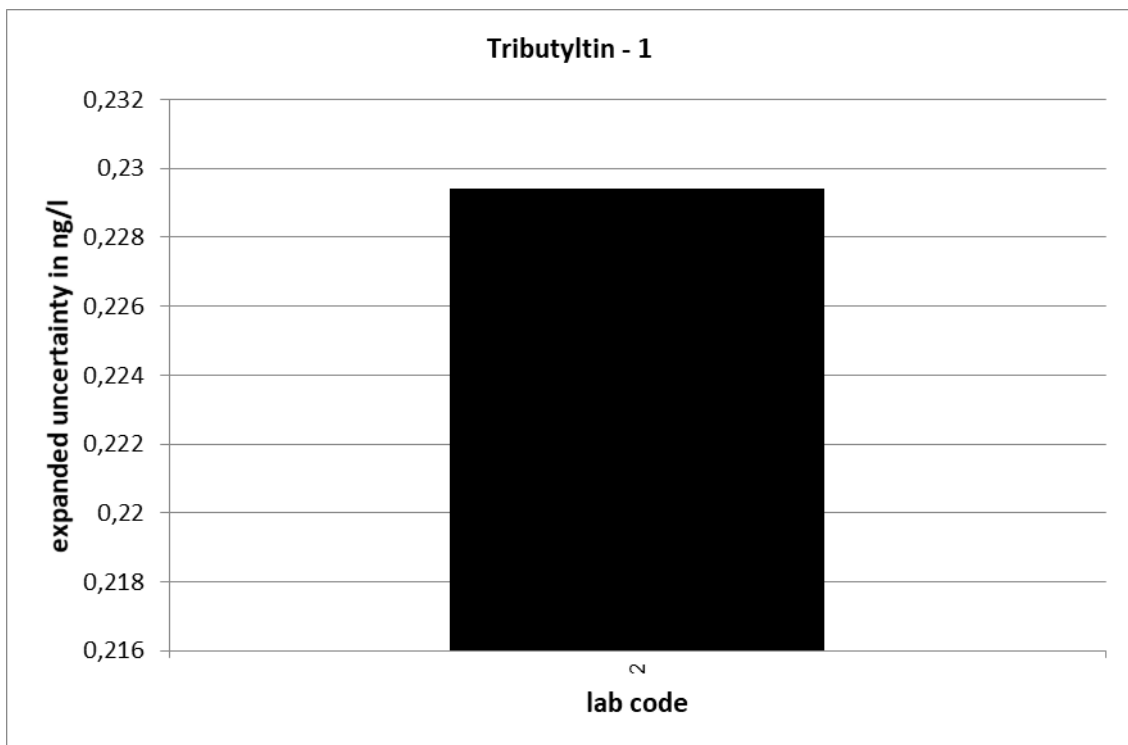
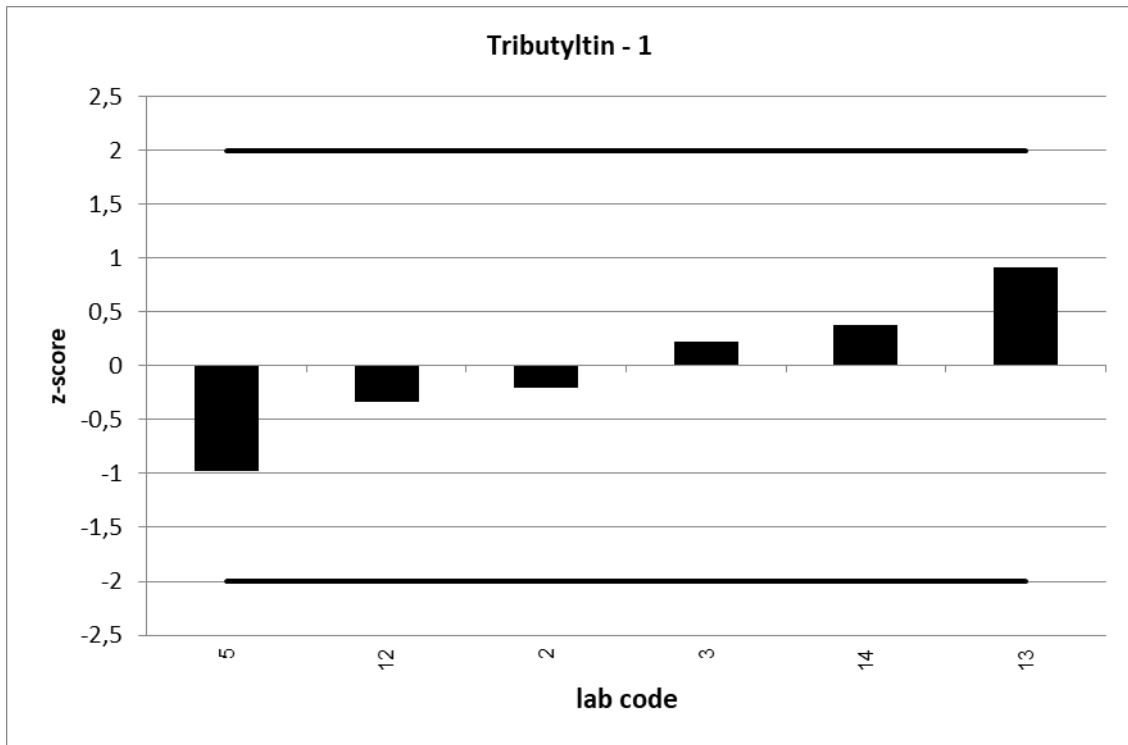
25 % is used as standard deviation for proficiency assessment.

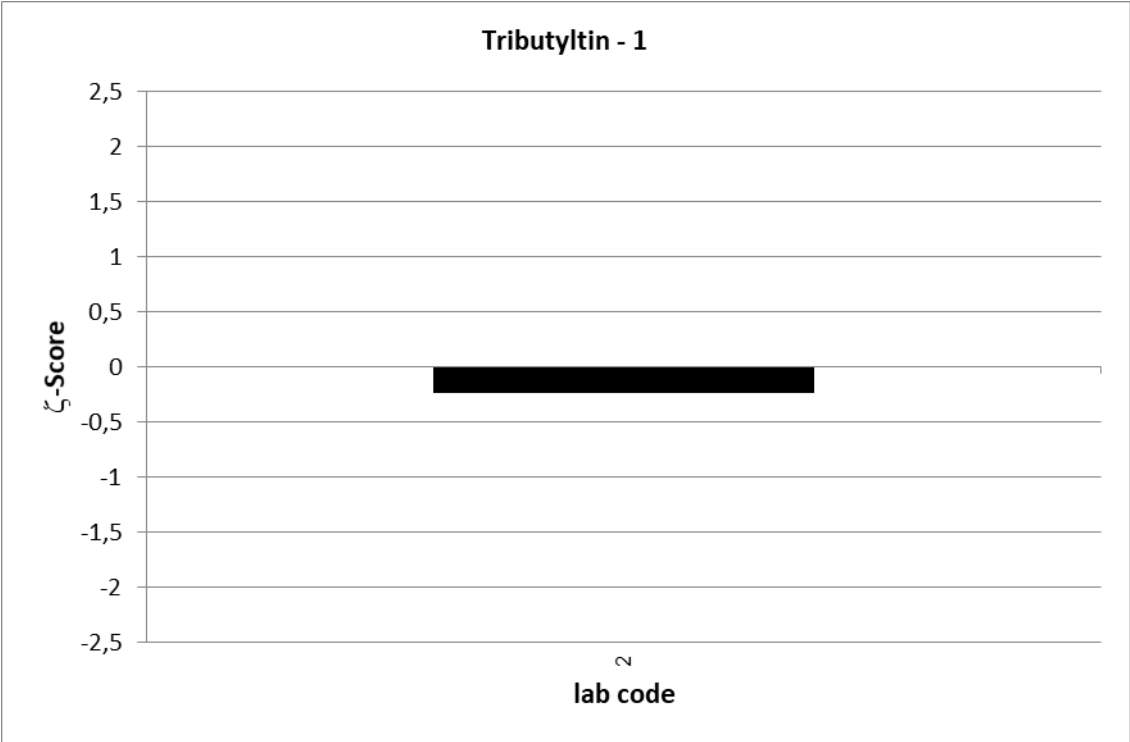
| UKWIR PT 14/21 | | Tributyltin - 1 | | | |
|------------------------------|---------------|-----------------|---------|---------|------------|
| assigned value [ng/l]* | | 0,7287 ± 0,2252 | | | |
| upper tolerance limit [ng/l] | | 1,093 | | | |
| lower tolerance limit [ng/l] | | 0,3644 | | | |
| lab code | result [ng/l] | ± | ζ-score | z-score | assessm.** |
| 2 | 0,691 | 0,229 | -0,2 | -0,2 | s |
| 3 | 0,77 | | | 0,2 | s |
| 5 | 0,55 | | | -1,0 | s |
| 12 | 0,668 | | | -0,3 | s |
| 13 | 0,896 | | | 0,9 | s |
| 14 | 0,7974 | | | 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



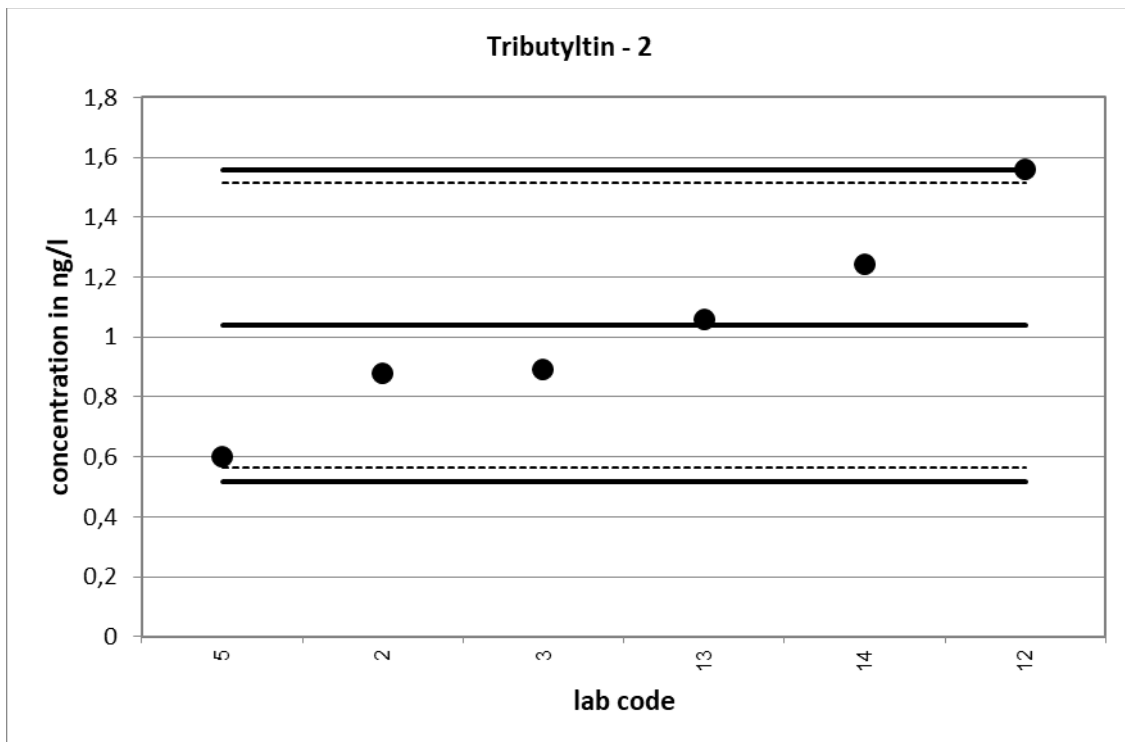


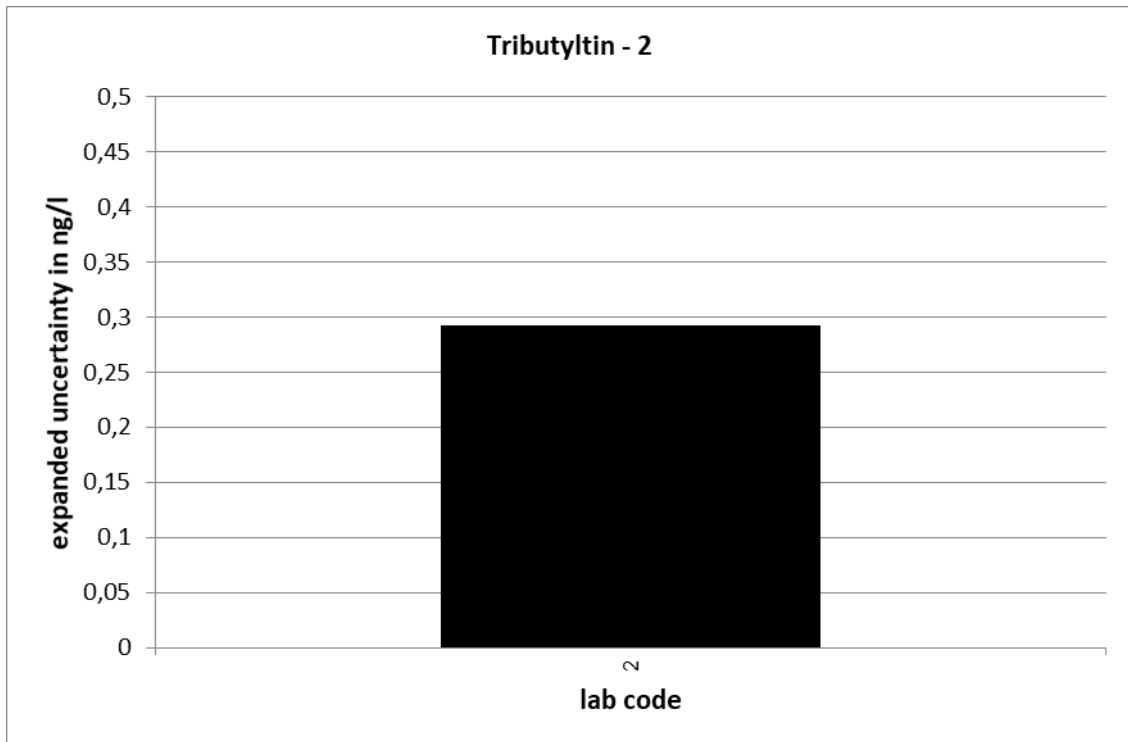
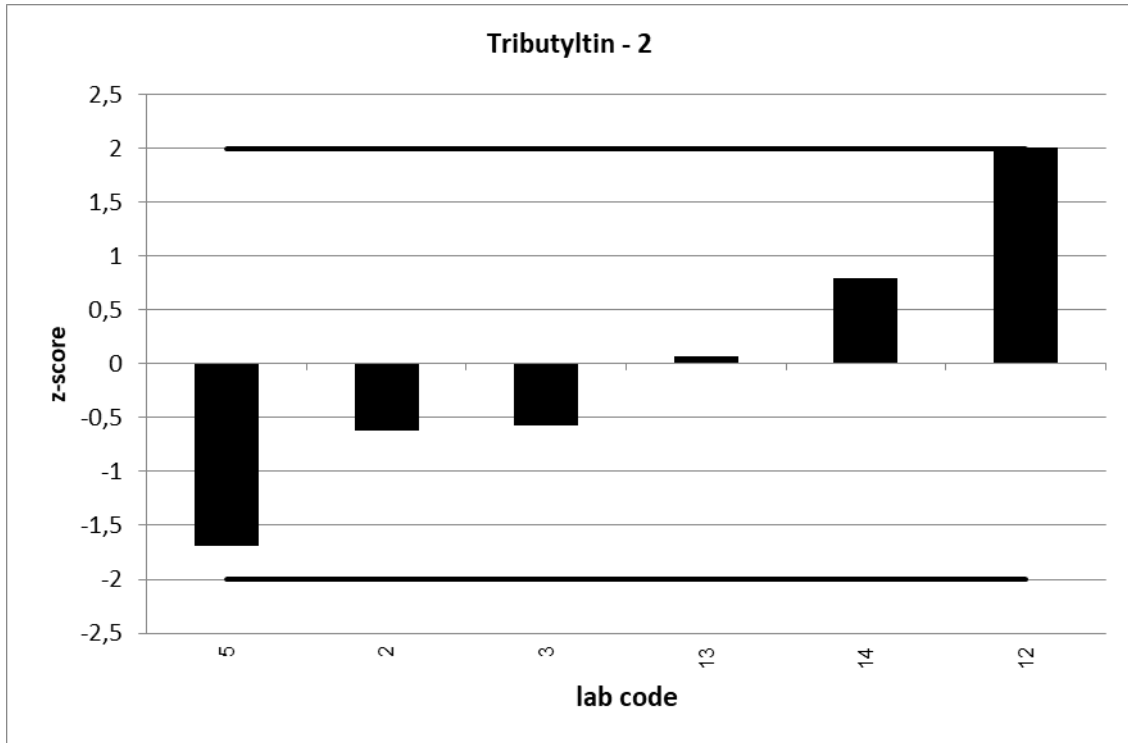


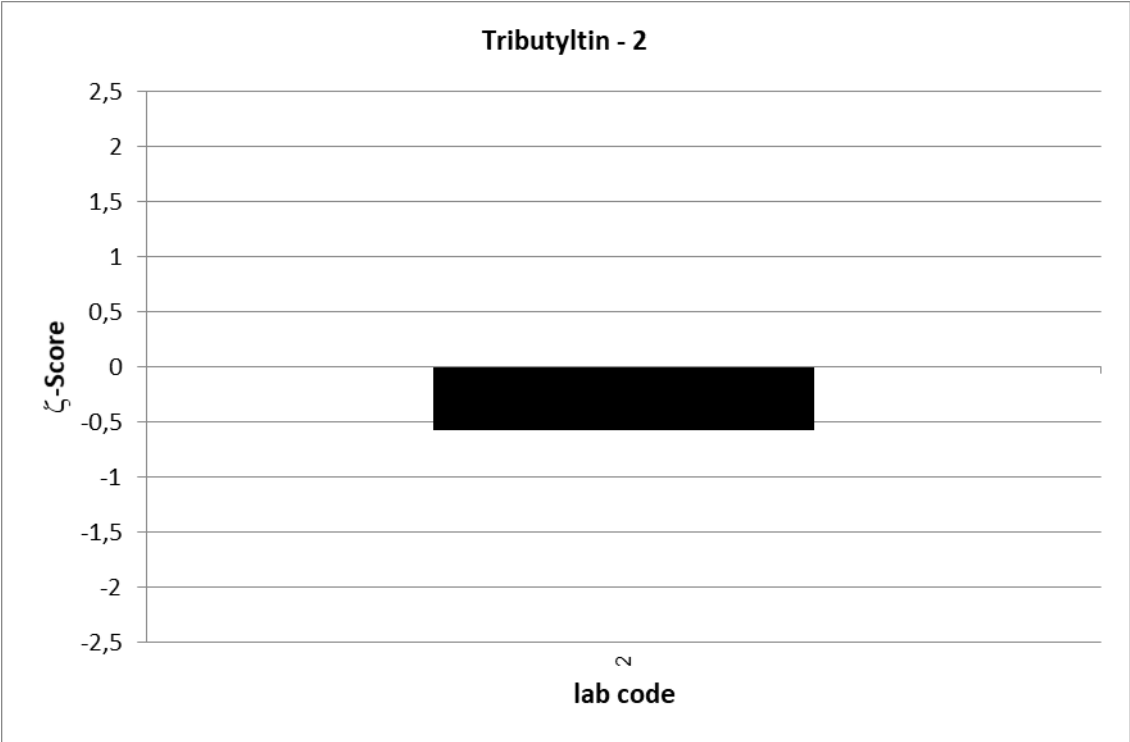
| UKWIR PT 14/21 | | Tributyltin - 2 | | | |
|------------------------------|---------------|-----------------|---------|---------|------------|
| assigned value [ng/l]* | | 1,039 ± 0,476 | | | |
| upper tolerance limit [ng/l] | | 1,558 | | | |
| lower tolerance limit [ng/l] | | 0,5193 | | | |
| lab code | result [ng/l] | ± | ζ-score | z-score | assessm.** |
| 2 | 0,879 | 0,292 | -0,6 | -0,6 | s |
| 3 | 0,89 | | | -0,6 | s |
| 5 | 0,6 | | | -1,7 | s |
| 12 | 1,56 | | | 2,0 | s |
| 13 | 1,058 | | | 0,1 | s |
| 14 | 1,245 | | | 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







| UKWIR PT 14/21 | | Tributyltin - 3 | | | |
|------------------------------|---------------|-----------------|---------|---------|------------|
| assigned value [ng/l]* | | 1,306 ± 0,252 | | | |
| upper tolerance limit [ng/l] | | 1,96 | | | |
| lower tolerance limit [ng/l] | | 0,6532 | | | |
| lab code | result [ng/l] | ± | ζ-score | z-score | assessm.** |
| 2 | 1,25 | 0,415 | -0,2 | -0,2 | s |
| 3 | 1,2 | | | -0,3 | s |
| 5 | 1,2 | | | -0,3 | s |
| 12 | 1,93 | | | 1,9 | s |
| 13 | 1,082 | | | -0,7 | s |
| 14 | 1,4292 | | | 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

